VOL. XXIII 1913

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY.

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TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

157559

VOLUME XXIII

TWENTY-THIRD GENERAL MEETING

ATLANTIC CITY, APRIL 3, 4, 5, 1913

PUBLISHED BY

THE AMERICAN ELECTROCHEMICAL SOCIETY

LEHIGH UNIVERSITY, SOUTH BETHLEHEM, PA.

1913.

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VOLUME XXIII. 1913.

TRANSACTIONS

OF THE

AMERICAN ELECTROCHEMICAL SOCIETY

PROCEEDINGS

CONDENSED MINUTES OF THE TWENTY-THIRD GENERAL MEETING OF THE SOCIETY, HELD AT ATLANTIC CITY, N. J., APRIL 3, 4 AND 5, 1913.

Number of members registered, 84; guests, 59; total, 143.

All sessions were held in the Solarium of the Hotel Traymore.

PROCEEDINGS OF WEDNESDAY, APRIL 2d.

The Board of Directors met at 8.30 P. M. at the Hotel Traymore. The annual report of the Secretary and Treasurer, and other actions there taken, aside from routine business, will be found immediately following these proceedings.

PROCEEDINGS OF THURSDAY, APRIL 3d.

The Annual Business Meeting of the Society was called to order at 11.00 A. M. in the Solarium of the Hotel Traymore, Dr. W. Lash Miller, President, in the chair.

The reading of the Minutes of the Twenty-second General Meeting was dispensed with, the Minutes being approved as printed in Volume XXII of the Transactions.

The report of the Board of Directors, including those of the Secretary and Treasurer, was read by the Secretary, and accepted for publication in the proceedings of the meeting, to which it is appended.

Briefly, this report shows a total membership of 1,350 at the close of 1912, a net gain of 29 during the year. The financial report shows a surplus of receipts over expenditures of $549.93, with $1,032.50 added to the permanent investment account. The net assets of the Society at the close of 1912 were: Cash on hand, $794.16; permanent investment, $5,621.11; total, $6,415.27.

The report was adopted, and a vote of thanks was extended to the Secretary for his labors in behalf of the Society.

In the absence of any of the Tellers of Election, the report of the annual election of officers was opened and read by the Secretary.

Report of the Tellers of Election.

To the American Electrochemical Society:

Gentlemen:—Following is the result of the count of ballots cast for officers of the American Electrochemical Society:

For President: E. F. Roeber 225, C. A. Doremus 1, E. R. Taylor 1, F. A. J. FitzGerald 1.

For Vice-Presidents: C. F. Burgess 193, S. A. Tucker 138, C. P. Townsend 135, W. H. Walker 67, F. J. Tone 64, Wm. Brady 39, H. M. Goodwin 25, W. C. Bray 2, E. F. Roeber 1.

For Managers: F. A. J. FitzGerald 133, J. W. Brown 125, C. G. Schluederberg 112, W. H. Walker 64, A. von Isakovics 58, W. C. Arsem 39, E. A. Sperry 36, T. F. Baily 30, P. McN. Bennie 28, O. P. Watts 20, M. deK. Thompson 14, R. H. Gaines 1, C. F. Burgess 1, S. A. Tucker 1, C. P. Townsend 1.

For Treasurer: P. G. Salom 223.

For Secretary: J. W. Richards 228.

Respectfully submitted,

Barry MacNutt,
S. S. Seyfert,
G. A. Roush.

South Bethlehem, Pa.,
March 18, 1913.

The Chairman then announced that, in accordance with the report of the Tellers, he declared as elected the following:

President (for one year): E. F. Roeber.

Vice-Presidents (for two years): C. F. Burgess, S. A. Tucker and C. P. Townsend.

Managers (for three years): F. A. J. FitzGerald, J. W. Brown and C. G. Schluederberg.

Treasurer (for one year): P. G. Salom.

Secretary (for one year): J. W. Richards.

President Miller congratulated these gentlemen on their election, then called on President-elect Roeber, who spoke as follows:

Mr. President, Ladies and Gentlemen: I feel very deeply that the presidency of the American Electrochemical Society is the highest honor that can come to me in my professional life. I realize that it is not an honor deserved, but I sincerely hope that it may be friendship deserved. I realize the responsibilities, and I see the opportunities.

During the eleven years of the existence of the Society it has assumed a truly international character in its membership, its work and its prestige. The fact that we are to have our meeting next year in Denver, Colorado, will give an opportunity somewhat to broaden the national character of the Society by emphasizing that electrochemistry is needed as much in the West as in the East.

In accepting the presidency I need the good will and friendship and support of every member—

President Miller: You have that.

Dr. Roeber: I ask for it, and I rely on it. I thank you with all my heart. (Applause.)

The business part of the session being concluded, the discussion of papers was taken up, and papers were presented by the following, and discussed as printed in these Transactions:

Irving Langmuir, and F. A. J. FitzGerald and A. T. Hinckley (read by F. A. J. FitzGerald).

In the afternoon the meeting was called to order at 2.15, and papers were presented by the following:

J. W. Richards, C. W. Bennett and H. N. Gilbert (read by C. W. Bennett), Reinhard Beutner, and C. W. Bennett and C. O. Brown (read by C. W. Bennett).

PROCEEDINGS OF FRIDAY, APRIL 4th.

Friday morning and afternoon were occupied by an excursion to Philadelphia. In the morning the plant of the Crucible Steel Castings Co., at Lansdowne, Pa., was visited, where a Roechling-Rodenhauser electric furnace was seen.

The visiting members and guests were given a complimentary luncheon at the University of Pennsylvania. The address of welcome, by Provost Edgar F. Smith, on behalf of the University, was responded to by President-elect E. F. Roeber for the Society.

In the afternoon the party divided, some going to the Harrison Chemical Works to see the manufacture of paint pigments and contact sulfuric acid, others going to the works of the United Gas Improvement Co., at Point Breeze, to see the manufacture of illuminating gas and water gas.

In the evening at 8.30 Prof. Frank B. Kenrick, of the University of Toronto, gave an experimental lecture on "Hyperbasis" in the Solarium of the Hotel Traymore. A description of the experiments performed will be found elsewhere in this Volume.

PROCEEDINGS OF SATURDAY, APRIL 5th.

The meeting was called to order at 11.00 A. M. by President Miller, who then delivered his Presidential Address, opening the Symposium on the Electrodeposition of Metals, as printed in full in these Transactions.

In the Symposium on Electrodeposition of Metals, which occupied the entire day, except for a short intermission for luncheon, papers were presented by F. C. Frary, O. P. Watts, F. C. Mathers, E. F. Kern and C. W. Bennett (two papers), which, with the discussion, are printed in full in these Transactions.

The members of the American Electroplaters' Society were invited to attend the Symposium and take part in the discussion, and a number of their members were present.

The following committees were appointed:

On motion of Prof. J. W. Richards, Mr. F. A. Lidbury (Chairman) and Mr. Albert H. Hooker were appointed a Committee on Occupational Diseases in the Chemical Trades, with power to add a third member, to co-operate with a similar committee of the American Chemical Society.

On motion of Dr. W. D. Bancroft the following members

were appointed a committee to co-operate with a similar committee of the American Electroplaters' Society in preparing a report on the whole subject of electroplating: W. D. Bancroft, Chas. H. Proctor and Geo. B. Hogaboom, with power to add to their number. Later the following were added to this committee: C. W. Bennett, F. C. Frary, F. A. Lidbury and F. C. Mathers.

The Secretary presented the following resolutions, which were duly seconded and passed:

Mr. President and Gentlemen: I move that the sincere thanks of this Society be extended and expressed to the Crucible Steel Casting Company, of Lansdowne, Pa.; Provost Edgar F. Smith and the authorities of the University of Pennsylvania; Harrison Brothers Company, of Philadelphia; the United Gas Improvement Company, of Philadelphia; Prof. F. B. Kenrick, of Toronto, and the Philadelphia Local Committee, for their hospitality, invitations and contributions towards the success of this meeting of the Society.

The Twenty-third General Meeting of the Society was then declared adjourned.

ANNUAL REPORT OF THE BOARD OF DIRECTORS.

To the Members of the American Electrochemical Society:

We submit herewith the annual reports of the Secretary and the Treasurer for the year 1912, the former containing the detailed financial statement of receipts and expenditures.

The increase in the number of members during the year 1912 was 29, the membership at the end of the year being 1,350. Eighteen members have been elected since the first of the year, and there are 14 applications on file awaiting action of the Board.

The financial status of the Society during 1912 remained satisfactory. The excess of receipts above expenditures was $549.93. A $1,000 bond, bearing 5 percent interest, and costing $1,032.50, was added to the permanent investment fund. The equity of the Society in the bonds now held amounts to over $5,600.

The following are the more important actions taken by the Board of Directors during the past year:

On January 27th the Secretary was authorized to print 2,300 copies of the General Index to Volumes I to XX, and to distribute it *gratis* to all members and purchasers of complete sets.

On March 23d the formation of the Pittsburgh Section was authorized to include members residing within a radius of fifty miles of Pittsburgh.

On April 17th it was ordered: "That a sum not exceeding $250.00 be placed at the disposition of a committee of three, to be appointed by the President, to be applied to the furtherance of scientific experimental research during the year 1912-1913. The committee is to advertise this matter in the Bulletin, receive applications for such financial assistance, make grants to such member or members as it may select, and require the results of such assisted research to be presented in proper form to the Society."

The By-Laws of the Society were amended as follows:
Section 3, Paragraph 3:

Add at end of Paragraph 3: "It shall be the further duty of the Secretary to organize and maintain means for securing the submission of papers to the Publication Committee."
Section 4:

Delete Paragraph 1 relating to the "Committee on Papers.'" Substitute the following for the paragraph relating to the Publication Committee:

"The Publication Committee shall consist of a Chairman, the President *(ex-officio)*, the Secretary *(ex-officio)* and four members. The Chairman of the Committee, to serve for one year, and two members, to serve for two years, shall be appointed yearly by the incoming President, subject to the approval of the Board of Directors. (In the first instance four members shall be appointed, two to serve for two years, and two to serve for one year.) Retiring members shall be eligible for reappointment. Vacancies arising on the Publication Committee shall be filled by appointment by the President, subject to the approval of the Board of Directors.

"The Publication Committee shall meet at each general meeting of the Society, at which time it shall set a date prior to which papers for the next meeting may be submitted. It shall pass on all papers so submitted, and shall have complete discretion as to what papers shall be accepted for presentation at the meetings of the Society; provided, however, that any member may appeal

to the Board of Directors against any decision of the Committee in respect to a paper submitted by that member.

"The Committee shall deal with all papers submitted as promptly as possible, and shall, where desirable, assist authors by suggestions which would improve the form of their papers as submitted.

"No member of the Committee shall pass on any paper of his own.

"The Committee shall have charge of the publication of the Transactions of the Society, and shall decide what papers shall be published in the Transactions. The editing of the Transactions shall be in the hands of the Committee.

"The Committee may assign work in connection with its duties to whatever member of the Society it sees fit.

"The Chairman of the Publication Committee shall keep a record of all papers submitted and of the action taken thereon. He shall report to the Board of Directors at each general meeting of the Society, and shall be responsible to the Board for the carrying out of the Committee's duties according to the By-Laws."

The following were adopted as

Rulings of the Board.

Acceptance of Papers.

"In general, no paper may be presented at a meeting of the Society unless it has been submitted in full prior to a date set by the Publication Committee as suitable to allow consideration by that Committee and the printing of advance copies before the meeting. In exceptional cases the President may authorize a paper, not previously submitted to the Publication Committee, to be read; such authorization will not, however, bind the Society or the Publication Committee in any way as to printing or publication.

"Papers of the following classes will be regarded as undesirable:

(a) Those containing no information or obviously incorrect information.

(b) Those containing only information already easily accessible.

(c) Those of an advertising nature not counterbalanced by adequate scientific information and treatment.

"Authors' abstracts of papers already published elsewhere may, however, be accepted for the purpose of discussion. Papers already published but not easily accessible will, if otherwise desirable, generally be accepted."

Advance Copies of Papers.

"Advance copies of such papers as are accepted by the Publication Committee will be printed as soon as possible for distribution before the meeting, and the author will receive twenty-five of these copies gratis, and have the right to order as many as he may wish at the regular rates."

Discussions.

"The Publication Committee will edit discussions; it shall not, however, change the meaning of any contributor's remarks, and the revised form of each contributor's remarks will be sent to him for approval; unless objection be raised within one week, it will be assumed that such is approved."

On May 25th, G. A. Roush, Assistant Professor of Metallurgy in Lehigh University, was appointed Assistant Secretary of the Society in place of W. S. Landis, resigned.

On September 9th the sum of $100 was appropriated to the International Commission for Publishing Annual Tables of Chemical and Physical Constants to apply as a subscription of $50 for the 1911 volume and $50 for the 1912 volume. Messrs. Taylor (Chairman), Doremus, Marvin, Brown (O. W.) and Schleuderberg were appointed to represent the Society at the Fourth National Conservation Congress in Indianapolis, Ind., October 1-4, 1913.

On October 26th an invitation from the Panama-Pacific Exposition to hold one of the 1915 General Meetings in San Francisco was considered and accepted, the date to be arranged later.

The Board of Directors has arranged for the Fall Meeting of the Society to be held in Denver, and hopes that members will support this venture by arranging their summer vacation so as to include Denver on the way home the first week in September. Our local members are very enthusiastic, appreciate our favoring them with the meeting, and promise us the most interesting meeting and visits which the Society has ever attended.

SECRETARY'S ANNUAL REPORT.

To the Board of Directors of the American Electrochemical Society:

GENTLEMEN:—In 1912 the Society held two General Meetings, one in Boston, April 18th, 19th and 20th, at which the attendance was 102 members and 67 guests, total 169; the second in New York City, in Joint Session with Section Xa: Electrochemistry, of the Eighth International Congress of Applied Chemistry, September 7th, 9th and 10th, at which there were registered 134 members and 28 guests, total 162. The Transactions of the Spring Meeting include 41 papers; those of the Fall Meeting 37 papers.

In 1912 there were issued and distributed to our members two Volumes of the Transactions—Volume XX, the Transactions of the Toronto meeting of September 21-23, 1911, and Volume XXI, Transactions of the Boston meeting of April 18-20, 1912. These Volumes contain 499 and 588 pages, respectively.

The Transactions of the New York meeting of September 7-10, 1912, were issued as Volume XXII, on March 22, 1913, containing 515 pages.

The edition of each of the 1912 Volumes was 1,500 copies bound in cloth for distribution to our members; 50 extra copies in sheets for distribution in pamphlet form to authors of papers; 250 copies bound in paper for distribution to the Faraday Society; and 500 copies sewed, ready for binding, to be kept in stock.

Complete sets of the Transactions are still on hand, but the stock is diminishing rapidly, and Volumes I and III will be hereafter sold at a double price, according to action of the Board of Directors.

A General Index of Volumes I-XX, 1902-1911, has been prepared and is now in the hands of the printer. On the authorization of the Board of Directors this will be sent *gratis* to all members of the Society.

The stock of Volumes on hand December 31, 1912, was as follows:

Volume	Bound in Cloth	Bound in paper or stitched ready for binding	Total
I	185	12	197
II	209	0	209
III	117	0	117
IV	146	234	380
V	96	234	330
VI	112	239	351
VII	113	247	360
VIII	130	248	378
IX	129	275	404
X	137	257	394
XI	130	261	391
XII	133	266	399
XIII	150	219	369
XIV	261	253	514
XV	257	222	479
XVI	25	522	547
XVII	192	518	710
XVIII	201	519	720
XIX	95	533	628
XX	77	535	612
XXI	94	559	653
Total			9,142

Condition of the Society in regard to Membership in 1912:

Members January 1, 1912		1,321
Elected and qualified as Members in 1912		107
Reinstated after being dropped for non-payment of dues		1
		1,429
Resignations in 1912	22	
Deaths in 1912	9	
Dropped for non-payment of dues	48	
	—	79
Members December 31, 1912		1,350
Net gain in membership in 1912		29

Financial Statement.

January 1, 1912, to December 31, 1912.

RECEIPTS.

Entrance Fees	$ 535 00
Current Dues	6,403 50
Sales of Publications	1,101 59
Advertisements	517 50
Membership Certificates	23 00
Sales of Society Pins	20 00
Interest on Investments and Bank Deposits	374 36
Temporary Loan from J. W. Richards	250 00
Research Award Returned by H. K. Richardson	75 00
	$9,299 95

EXPENDITURES.

Office Printing		$ 373 53
Postage		671 00
Publications		4,448 57
Salary, Secretary and Stenographer		871 92
Salary, Assistant Secretary		300 00
Office Expenses		324 75
Engrossing Membership Certificates		8 61
Appropriations to Sections		100 00
Storage		75 20
Permanent Investment		1,032 50
Accrued Interest on Bond		19 17
Expenses of Meetings		469 15
Faraday Transactions: Payment for Extra Copies		460 62
Commission on Advertisements		52 50
Assisted Research Awards		150 00
Internat. Committee for Annual Table of Constants		100 00
Appropriation for Symposium		75 00
Repayment of loan from J. W. Richards		250 00
		$9,782 52
Excess, Expenditures above Receipts		$ 482 57
Permanent Investment	$1,032 50	
Loss in Cash Balance	482 57	
Gain in Assets		549 93

ASSETS, JANUARY 1, 1912.

Cash balance, January 1, 1912—On deposit		$1,226 73
Cash box		50 00
Bonds held by the Society (cost price)	$5,088 61	
Ferro Boron prize, held in trust	500 00	
Equity of Society in above bonds		4,588 61
		$5,865 34

ASSETS, DECEMBER 31, 1912.

Cash balance, December 31, 1912—On deposit		$ 744 16
Cash box		50 00
Bonds held by the Society (cost price)	$6,121 11	
Ferro Boron prize, held in trust	500 00	
Equity of Society in above bonds		$5,621 11
		$6,415 27
Gain in assets for year 1912		$ 549 93

Jos. W. Richards, *Secretary.*

TREASURER'S ANNUAL REPORT

FOR THE YEAR 1912.

Cash balance, January 1, 1912	$1,276 73	
Total receipts as per statement attached, January 1, to December 31, 1912	9,299 95	
Total for 1912		$10,576 68
Total expenditures		9,782 52
Balance, December 31, 1912		$ 794 16
Balance in E. P. Wilbur Trust Co.	$1,072 77	
Balance in Commonwealth T. I. and T. Co.	69 55	
Balance in cash drawer	50 00	
	$1,192 32	
Less vouchers not in (526-529)	398 16	
Balance, December 31, 1912		$ 794 16

PEDRO G. SALOM,
Treasurer.

We have examined the accounts of the American Electrochemical Society, verified the receipts and expenditures submitted herewith, and find them correct.

HENRY G. MORRIS,
S. S. SADTLER,
Auditors.

MINUTES OF MEETING OF BOARD OF DIRECTORS

The meeting was held in the Hotel Traymore, Atlantic City, New Jersey, Wednesday, April 2, 1913, at 8.30 P. M.

Present in person: Miller (presiding), Whitney, FitzGerald, Isakovics, Lidbury, Bancroft, Hering, Roeber, Saunders, Salom, Richards. Present by proxy: Walker, Smith, Tucker, Kahlenberg.

The minutes of the meeting of February 21st were approved as printed.

On motion it was ordered that the Ferro-Boron Prize of $500 be returned to the Pacific Coast Borax Company with interest since the closing of the competition and report of the committee thereon.

On motion the President was authorized to expend a sum not exceeding $200 to defray the expenses of compiling symposiums in connection with the next two meetings of the Society.

On motion the sum of $250, in *toto,* is placed at the disposal of the Committee for Assisting Research, the fact of the said sum being available in the year 1913-14 to be advertised in the Bulletin.

The Publication Committee made a report, which was accepted and placed on file.

It was moved that the President appoint a Committee on Arrangements for the September Meeting in Denver.

It was moved that the Board favors the holding of a meeting in the South in the Fall of 1914, but does not at present commit the Society to such action.

It was moved that the Society co-operate with the International Electrical Congress at the 1915 meeting in San Francisco.

The Secretary made his annual report for the year 1912. The Treasurer made his annual report for the year 1912, duly audited. These reports will be printed in full in the Proceedings of the Twenty-third General Meeting, in Volume XXIII of the Transactions.

Adjourned.

Jos. W. Richards,
Secretary.

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Guests.

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Chas. W. Bailer, Philadelphia.
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Samuel Barr, Philadelphia.
E. H. Bedell, New York.
R. S. Bicknell, New York.
H. Bloodsworth, Lansdowne, Pa.
J E. Breckenridge, Woodbridge, N. J.
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deCourcy B. Browne, New York.
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Earl Eastman, Atlantic City, N. J.
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A. S. White, Philadelphia.
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Members Elected and Qualified.

October, 1912—April, 1913.

October 26, 1912.

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John A. Coyle, Bridgeton, N. J.
C. H. Vom Baur, New York City.
Joel H. Hildebrand, Philadelphia.
H. G. Dorsey, Dayton, Ohio.
Fin Sparre, Wilmington, Del.

November 30, 1912.

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Yoshio Tsuboi, Akitaken, Japan.
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December 28, 1912.

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Frederick G. Cottrell, San Francisco, Cal.
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Cho Yang, South Bethlehem, Pa.

January 25, 1913.

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February 21, 1913.

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The Presidential Address, introducing the Symposium on Electrodeposition of Metals, at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913.

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THE ELECTRODEPOSITION OF METALS

By W. Lash Miller.

In opening this symposium, I wish first of all to convey the hearty thanks of the Society to our members, Messrs. Bancroft, Bennett, Frary, Kern, Mathers and Watts, who have carried through the laborious task of collecting the data that are in our hands today. To make this collection it was necessary to go through the patent literature, and to search monographs, abstract journals and text-books of inorganic chemistry, electrochemistry, electroanalysis, electroplating and electrorefining for sources of information, and then to consult the original articles in dozens of scientific and technical journals. No attempt has been made to give only the "good" recipes; in photochemistry, as is well known, the art of photography has far outstripped the science, and here too it may be found that some "obviously" silly addition to the bath, recommended by a technical man, may in practice have a beneficial effect for reasons unsuspected and unexplained.

The compilers, of course, accept no responsibility except for the correctness of their abstracts. Their work has furnished us with a summary of permanent value and a basis for today's discussions. Our thanks are due them, and are hereby tendered, for all the trouble they have taken.

Our subject of today was brought before this Society nine years ago at one of its joint meetings with the Fifth International Electrical Congress at the St. Louis Exposition, in a paper by Bancroft[1] on "The Chemistry of Electroplating." In this paper the author, among other matters, compared the structure of metals deposited electrolytically by heavy currents with the structure of precipitates produced rapidly by purely chemical means, and in this analogy found the only explanation we yet

[1] Bancroft, These Transactions, 6, 27-43 (1904).

have of the direct effect of current density on the structure of the deposit.

Now, nine years later, this parallelism between "electrochemical" and purely chemical processes,[2] which Bancroft was one of the first to emphasize, is generally recognized; and some striking new instances have been found by Skrabal[3] in his study of the reduction of the chromates; it is, moreover, at the bottom of all the explanations recently put forward to account for certain puzzling voltages observed at the electrodes during electrolysis, which is the subject I have chosen to speak on today.

If the electromotive force needed to send a heavy current through a given electrolytic cell is greater than that required to send a light current by more than the product of the current-difference into the resistance of electrolyte and wiring, the cell is said to be "polarized" by the current. The same word is frequently made use of when it is found that a higher voltage is needed to bring about a given reaction—say, the liberation of hydrogen—at an electrode of one material, say mercury, than when another material, say platinum, is employed. Two causes for such polarization have long been recognized. The first is the formation of a precipitate or film which may shut off the current altogether, as with anodes of aluminum or tantalum,[4] or which may cut down the current and so permit the precipitate to dissolve, giving rise to periodic phenomena, as in the electrolysis of sodium sulphide[5] or of some nickel salts,[6] or which finally, while letting the current pass, may protect the metal from solution and so render it "passive," as with anodes of lead[7] and tin[8] in solutions of caustic soda. The second long-recognized cause of polarization is the electromotive force due to concentration changes set up at the electrodes by the current.

Other causes, of course, have been suggested; but, until recently, acting on what Mach calls the principle of "economy" in

[2] See also, Luther, Zeit. f. Elektrochem., 8, 646 (1902), and Bancroft, These Transactions, 8, 33 (1905).

[3] Skrabal, Zeit. f. Elektrochem., **14**, 529 (1908).

[4] v. Bolton, Zeit. f. Elektrochem., **11**, 49 (1905).
Kuessner, Zeit. f. Elektrochem., **16**, 769 (1910).

[5] Koelichen, Zeit. f. Elektrochem., **7**, 629 (1901).
Küster, Zeit. anorg. Chem., **46**, 113 (1905).

[6] Thiel u. Windelschmidt, Zeit. f. Elektrochem., **12**, 737 (1906), and **13**, 317 (1907).

[7] Elbs u. Forsell, Zeit. f. Elektrochem., 8, 760 (1902).

[8] Foerster u. Dolch, Zeit. f. Elektrochem., **16**, 599 (1910).

science,[9] electrochemists have endeavored to refer all cases of polarization to one or the other of the two classes just defined. It was not always easy. Experiments with anodic mirrors,[10] for instance, have discredited the oxide-film theory of the passivity of iron, while the concentration-cell explanation loses plausibility when it assumes such concentrations as ten tons of hydrogen per liter to "explain" the polarization of mercury in normal sulphuric acid.[11] Still, it is always possible to assume "invisible films" and endow them with any properties desired; and equations which lead to impossibly high concentrations awake in some minds a feeling of reverence rather than criticism; so that the necessity for new explanations was recognized only when it appeared that concentration changes at the electrodes may be calculated from the laws of diffusion, and that in certain instances they are wholly insufficient to account for the polarization observed.

The first to make such calculations was Weber;[12] his results, like those of his successors, Warburg[13] and Sand,[14] were based on the assumption that in the experimental work all convection—whether due to stirring, vibration, heating, evolution of gases, or change of specific gravity in the solutions—was strictly excluded. The great advance in the theory of diffusion which has freed experimenters from such difficult conditions was made in Noyes and Whitney's[15] paper on the rate of solution of solids; and their theory of diffusion through an adherent liquid film,[16] applied by Nernst,[17] Brunner[18] and Merriam,[19] has led to quick and reliable laboratory methods of determining the concentrations sought.[20]

[9] Mach, Popular scientific lectures, Chicago, Open Court Pub. Co. (1895).

[10] Müller u. Königsberger, Physik. Ztschr., **5**, 413, 797 (1904); Zeit. f. Elektrochem., **13**. 659 (1907).

[11] 0.42 volt, according to Müller, Zeit. anorg. Chem., **26**, 1 (1900): higher according to Coehn u. Danneberg, Zeit. phys. Chem., **38**, 609 (1901), and Caspari, Zeit. phys. Chem., **30**, 89 (1899).

[12] Weber, Wied. Ann., **7**, 536 (1879).

[13] Warburg, Wied. Ann., **67**, 493 (1899).

[14] Sand, Zeit. phys. Chem., **35**, 641 (1900); Phil. Mag., [6] **1**, 45 (1901).

[15] Noyes and Whitney, Zeit. phys. Chem., **23**, 689 (1897).

[16] A similar hypothesis has just been introduced into the theory of the conduction of heat in gases, and promises to be equally fruitful. See Langmuir, this vol., p. 299.

[17] Nernst, Zeit. phys. Chem., **47**, 52 (1904).

[18] Brünner, Zeit. phys. Chem., **47**, 56 (1904).

[19] Nernst u. Merriam, Zeit. phys. Chem., **53**, 235 (1905).

[20] A full treatment of the mathematical theory of the concentration changes at the electrodes brought by direct, interrupted, or alternating current, which includes the case of non-instantaneous reactions between the primary products of electrolysis and the other constituents of the solution, is given by T. R. Rosebrugh and W. Lash Miller, Jour. Phys. Chem., **14**, 816-884 (1910).

The inadequacy of the film and concentration explanations once recognized, what is the nature of the new explanations now advanced? Again the parallelism between electrolytic and purely chemical reactions is appealed to: The growth of copper at the cathode is compared with that of crystals in an undercooled solution; reactions at the electrode hitherto supposed instantaneous are seen to take their time like others; hypothetical hydrated ions are introduced, requiring time to give up their water; "intermediate" compounds of all kinds are assumed—in short, the whole collection of viewpoints and hypotheses built up by the study of chemical kinetics is transferred bodily to electrochemistry. One thing at least is gained: The old, undue simplicity is gone; while Faraday's and Hittorf's laws, of course, remain, and the principles of thermodynamics are as valid as ever, it is now recognized, never again to be forgotten, that electrochemical processes like those of pure chemistry are subject to the Bancroft-Ostwald law as well, according to which the thermodynamically "most probable" reaction is in practice perhaps the least likely to occur.[21]

Smale[22] thought years ago, and all thought with him, that he had determined the electromotive force of the reversible oxyhydrogen cell to be 1.075 volt; Haber[23] shows that 1.23 volt is nearer the truth. Much work[24] was done to clear the matter up, and now it seems that the electrodes—even "unattackable" platinum and iridium—are converted during electrolysis into oxides or hydrides, by whose subsequent decomposition oxygen and hydrogen are formed.[25] At all events, such substances have been prepared,[26] and prove to have the properties required. The assumption that these oxides are only slowly formed explains the need for waiting several days[27] before the "chromic acid electrode" attains its final electromotive force, while the observation often made that platinum or iridium serves "better" than gold[28]

[21] Bancroft, Jour. Phys. Chem., **1**, 137 (1896); see also Wald, Zeit. phys. Chem., **24**, 509 (1897); Ostwald, Zeit. phys. Chem., **22**, 306 (1897).

[22] Smale, Zeit. phys. Chem., **14**, 577 (1894); **16**, 562 (1895).

[23] Haber, Thermodynamik technischer Gasreaktionen, p. 161 (1905).

[24] Luther, Zeit. f. Elektrochem., **13**, 290 (1907).

[25] Lorenz, Zeit. f. Elektrochem., **14**, 78 (1908).

[26] Wöhler, Zeit. f. Elektrochem., **17**, 98 (1911).

[27] Scobai, Zeit. f. Elektrochem., **9**, 879 (1903).

[28] Crotogino, Zeit. anorgan. Chem., **24**, 245 (1900).

for oxidation cells may be due to the lack of a suitable series of gold oxides or to the slower rate at which they may be formed.

The conception of the electrode process thus has changed. No longer does the H^+ sign simply lose its *plus*—or the ion its charge, if that form of symbolism be preferred—and then uniting two by two leave the electrode with the exact potential most convenient for thermodynamical computations, all over in an instant. Now we must think of purely chemical reactions, of series of indefinite hydrides, or oxides, as the case may be, slowly reaching equilibrium with the solution.

The only reliable test of a conception is its fruitfulness, and Mills'[29] criterion of a good scientific hypothesis is that it may be tested. The point of view just set out suggested and offers a satisfactory explanation of some experiments carried out by students in the Toronto laboratory, to which I shall now refer.

If sulphuric acid, potassium bichromate and potassium iodide are dissolved in the right proportions in water, iodine is slowly liberated.[30] It must be obvious that in such a solution the electromotive force thermodynamically "necessary" to reduce the chromic acid is less than that required to reduce the iodine. In point of fact, however, if a cathode be introduced, it is the iodine, and not the chromic acid, that reacts. The "oxide theory" of the chromic acid electrode, taken together with Merriam's observation that the electrolytic reduction of iodine is practically instantaneous, gives the explanation. A gold electrode is most convenient, because platinum catalyses the reaction between chromic acid and iodide; the "oxide" explanation of this difference between the two metals has just been gone into, and it is hoped that measurements of the rate of catalysis may furnish a check.

Arsenic acid behaves just like chromic; in this case, moreover, conditions under which the reverse reaction can conveniently be studied are known,[31] and a few experiments served to show that an anode oxidized iodide instead of arsenious acid, in solutions where all the while iodide was being formed and arsenious

[29] "The hypothesis, by suggesting observations and experiments, puts us on the road to that independent evidence, if it be really attainable; and till it be attained, the hypothesis ought only to count for a more or less plausible conjecture." J. S. Mills, System of Logic, Book III, Chap. 14.

[30] De Lury, Jour. Phys. Chem., 7, 239 (1903).

[31] Roebuck, Jour. Phys. Chem., 6, 365 (1902); 9, 727 (1905).

acid destroyed by the "purely chemical" reaction. Particularly sharp results can be obtained with solutions where the two reactions are in equilibrium, working with low concentration of free iodine, as described by Roebuck,[32] but I shall not take up time with these details.

Perhaps the most interesting are the results obtained with iron.[33] Four years ago Mr. D. A. Welsh found that in solutions where iodide was slowly undergoing oxidation by a ferric salt, platinum accelerated the reaction, and a gold cathode reduced the iodine. The ferric salt thus behaves exactly like chromic acid. If the explanation is to be the same, a new formula for the electrolytic reduction must be used; $Fe^{+++} \rightarrow Fe^{++}$ will not serve any longer; intermediate steps have been left out.

More closely connected with our subject of today is the cathodic polarization observed by LeBlanc[34] with the oscillograph during electrolysis of the sulphates or nitrates of copper, nickel and silver. The study of these and similar cases has been continued by Reichinstein, who, working with direct current,[35] observed polarizations as high as 0.7 volt during the deposition of copper on a copper cathode in slightly acid solutions of copper sulphate, and has elaborated a theory to account for these results, based on the assumed primary formation of a hydrogen-copper alloy.

With apparatus constructed after Reichinstein's description,[36] Mr. Burt-Gerrans and Mr. Brant were able to reach polarizations of the same order as his, the deposit being pure copper and no hydrogen being evolved; in order to check the theoretical explanations offered, they repeated the experiments, adding a nickel salt to the solution. As the decomposition voltage of nickel sulphate is less than 0.6 volt higher than that of copper sulphate, it is hard to see how a deposit of alloy on the electrode, or delay in the dehydration of copper ions, or a deficiency of cuprous salt at the cathode, could interfere with the deposition of nickel if the electromotive force between solution and cathode were kept 0.7 to 0.8 volt higher than that needed (with low currents) to deposit

[32] Roebuck, *loc. cit.*, p. 392.

[33] See also Maitland, Zeit. f. Elektrochem., **12**, 264 (1906), and Nernst u. Merriam, *loc. cit.*

[34] LeBlanc, Abh. d. Deutschen Bunsen Ges., No. III (1910).

[35] Reichinstein, Zeit. f. Elektrochem., **18**, 850 (1912).

[36] Reichinstein, *loc. cit.*, p. 855.

copper. The wished-for voltage was maintained for fifteen minutes with a current of 0.44 ampere, but the deposit contained no trace of nickel. Similar experiments with the chlorides of copper and tin, and with the nitrates of silver and copper, likewise gave negative results.

Another explanation of the polarization must therefore be sought. Reichinstein's cathode consisted of a plate of copper covered with paraffin except for five square centimeters of one of its surfaces, in front of which—*i. e.*, directly between cathode and anode—and "extremely close to the paraffin-free surface," rotated a Witt's stirrer of glass. The siphon leading to the hydrogen electrode and the potentiometer circuit with which the polarization was measured entered the cell behind the cathode plate. It is obvious that, in order to find the true polarization with such an arrangement, the potentiometer readings must be corrected by subtracting something for the drop of potential along the (curved) path of the electrolysing current; the order of magnitude of this correction, however, cannot be estimated without knowledge of the dimensions of the apparatus. This correction will depend, for instance, on the distance between anode and cathode, and it will be the greater the larger the stirrer and the nearer it is to the cathode, the larger the anode surface, and the larger the paraffined margin around the cathode surface.

In the absence of such data the curves[37] themselves give a hint. Above 0.1 volt they are almost straight lines, voltage rising with current; and in Fig. 532[38] (which records a number of measurements with different solutions, made without disturbing the apparatus) their slopes are proportional to the specific resistances of the solutions used. These curves, then, suggest very strongly that the higher "polarizations" recorded would be substantially cut down by a suitable correction for the potential drop in the electrolyte, and, provisionally at least, may be regarded as confirming the negative result obtained in the nickel experiments.

If this turns out to be the case it would seem that there is still room for a very old-fashioned explanation of some cases of polarization side by side with the most modern developments of the chemical analogy!

[37] The ordinates record the uncorrected "polarization," and the abscissae the electrolysing current.

[38] *Loc. cit.*, p. 860.

A paper presented in the Symposium on Electrodeposition of Metals, at the Twenty-Third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913, President W. Lash Miller in the Chair.

THE ELECTRODEPOSITION OF GOLD AND SILVER

By Francis C. Frary.

The following paper, prepared at the request of the President of this Society, is intended to be a compilation of all recipes for plating gold and silver upon other metals by electrolytic processes, as far as such recipes could be found in the sources available to the author. None of the matter here presented is original, and the author assumes no responsibility for the truth of the statements made herein except that of a compiler who undertakes to do his work as accurately as possible. Acknowledgments are due to the Board of Directors of the Society for a grant of money for clerical help and to procure assistance in the search for the material involved, and to my assistant, Mr. Arthur C. Dennis, for his careful work in this connection. In order that others who may wish to supplement this article with a further search of the literature may know what journals have been covered here, a list of them and of the various handbooks and textbooks used is appended hereto. In the text the journals are referred to by their customary abbreviations, and the handbooks, etc., by the names of their authors, followed by the page number.

Introduction.

There seem to be three ways of coating metals with gold or silver. The oldest consisted in the application of a gold or silver amalgam to the object, with or without the use of gold or silver leaf, and subsequently volatilizing the mercury by heating. Several repetitions of this process were necessary to give a satisfactory coating, as the first coats were more or less absorbed or dissolved in the surface of the object. Such processes were purely mechanical, involving no electrolytic decomposition of chemical compounds. The second method consisted in the

preparation of a mixture (solution or paste) in which the gold or silver was in such a state that upon applying it to an object, preferably of copper or brass, the metal would be deposited upon the object in an adherent, if thin, coat. Since such deposition was naturally at the expense of the metal composing the object, part of which replaced the gold or silver in the mixture, it certainly involved the passage of an electric current through parts of the object, which may be considered as made up of an infinite number of small batteries, and this is strictly electroplating. The third method, developed naturally from the second as soon as men began to learn more about electricity, consisted in the electrodeposition of the metal from solution upon the object to be plated, which was made the cathode in a suitable bath. This comprises the processes coming under the head of ordinary electroplating processes. A fourth method involving the chemical reduction of the gold or silver from a solution by reducing agents therein, and its deposition upon any object immersed therein, is very useful for plating glass and similar substances, but does not come within the scope of this article.

In the recipes given below the weights and substances involved are as given by the original authors, except that where obsolete measures were used they have been either converted into parts by weight or else into their metric equivalent. The use of distilled water is assumed throughout the paper, but the quality of the chemicals involved is not so clearly defined. This is especially the case wherever potassium cyanide is involved, as this substance was commonly of a very low degree of purity in the early days of electroplating, being contaminated by large quantities of carbonate and cyanate, and usually by some ferrocyanide. Some handbooks of early days frankly admit that the commercial salt contained only about 50 percent of real cyanide; the quantities of this substance involved in the recipes from such times would therefore have to be diminished by a large and uncertain amount to make it possible to duplicate the solutions with modern commercial cyanide. Most recipes give directions for the preparation of the chloride of gold or nitrate of silver involved; these have been omitted except where they left in the finished solution an appreciable excess of the acids used, which would of course react with other constituents of the bath to form salts which

might influence the character of the deposit. Wherever weights of gold or silver are given, unless otherwise stated, they refer to the actual weight of the pure metal used, although it was in the form of an alloy or a salt.

So far as possible solutions which were intended to be used without a battery are so marked; they differ from solutions intended for use with a battery in that they must contain an agent capable of dissolving the metal of the object to be plated, but this solvent action must be slight, or else the deposit will not be adherent. For this reason baths intended for use as dips or pastes could, when in the form of clear solutions, be used with a battery; but many solutions intended for use with the battery could not be used for dipping or brushing on the object. Solutions intended for plating with a battery should have little if any solvent action on the objects to be plated, or else the deposited coat will not be adherent. In general, dipping or brushing with a suitable solution will give only a very thin coat of the metal, while with the use of the battery thicker coats may be obtained if desired.

Part I. Electrodeposition of Gold.

Simple Halide Baths.

Perhaps the simplest process, theoretically, of depositing gold on an object is that patented by Edison,[1] where the object to be plated is placed in an evacuated chamber together with an arc formed between electrodes of the metal to be deposited. The object is turned so that its different faces are presented to the arc, and is thus coated by the metallic particles shot off from the latter.

Another very simple process is represented by several formulas in all of which a gold solution is absorbed in small pieces of rag, preferably linen, and these dried and burned. The ashes are made to a paste with water, and rubbed on the object to be plated. A solution of plain gold chloride may be used for this method,[2] or a solution made by dissolving gold in a mixture of five parts nitric acid, two parts salammoniac and one-half part

[1] U. S. Pat. 526147, Sept. 18, 1894.
[2] Henley, p. 579.

saltpeter,[3] or the same solution containing one part of saltpeter instead of one-half part,[4] or a solution of 60 grains of gold and 10 to 12 grains of copper in two ounces of aqua regia.[5] A modification of this method[6] consists in precipitating the gold from its chloride solution by addition of a piece of copper or some ferrous sulphate solution, digesting the precipitate with "distilled vinegar," washing and drying. Apply as above.

Gold chloride is decomposed and gold deposited if any metal having a greater electrolytic solution tension than gold is immersed in the solution. This deposition is so rapid, however, that the coating of gold is non-adherent and powdery in most cases, although it is stated[7] that articles of iron, silver or copper can be given a thin coat of gold by immersion for a very short time in such a solution. Von Ruolz[8] states that plain gold chloride solutions give a powdery, non-adherent deposit when copper articles are dipped in them, but if hydrocyanic acid (2½ times the weight of the gold chloride) be added, and the mixture allowed to stand half an hour, the solution no longer corrodes polished copper, and can be used with a battery for the deposition of a good coat of gold. It is also stated[9] that an ethereal solution of gold chloride will give a good gilding if painted on polished steel. By electrolysis of a gold chloride solution with a very weak current Elsner[10] obtained a fair deposit of gold. Böttger[11] recommends the use of a 1 : 160 solution for this purpose, and states that it should be made as neutral as possible, and the object plated must be removed, rinsed and polished at the end of each minute of plating. Elsner[12] found that this solution was too strong and must be diluted to get the best results. He also emphasized the necessity of neutralizing the acid present with soda. De la Rive[13] also used the simple chloride of gold in a solution containing 40 to 80 grains per pound.

[3] Spon, **I**, 275.
[4] Watt and Philipp, p. 173; Henley, p. 577.
[5] Dingler Poly. J., **28**, 471 (1828).
[6] Henley, p. 579.
[7] Watt and Philipp, p. 167.
[8] Compt. rend., Oct., 1847, No. 16; Dingler Poly. J., **107**, 315 (1848).
[9] Sci. American (I), **6**, 106; Watt and Philipp, p. 167; Henley, p. 580; Sci. Am. Cyclopedia, p. 188.
[10] J. Prakt. Chem., **23**, 149.
[11] Frankfurter Gewerbefreund 1840, No. 10; Dingler Poly. J., **78**, 51 (1840).
[12] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, 1840; Dingler Poly. J., **80**, 144 (1841).
[13] Compt. rend., 1840, No. 14; Dingler Poly. J., **76**, 297 (1840); J. Prakt. Chem., **20**, 157.

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Stahl[14] uses a 1½ percent solution of gold chloride, a "neutralization bath" consisting of a solution of caustic soda at 6° Bé., and a "reduction bath" made by mixing equal parts of 90 percent alcohol and water, and dissolving pure hydrogen in this solution. Gilding is done by immersing the article in the gold bath, then moving it briskly in the neutralization bath, and finally immersing in the reducing bath. Besides these an "anti-reducer" is needed. This consists of rectified and rosinified turpentine 50 gm., and 10 gm. sulphur, boiled together to form a syrupy balsam, to which is added before use some oil of lavender, well-ground basic bismuth nitrate and the solution for gilding and silvering. The method of using this mixture is not clear.

Böttger[15] also suggested the use of the double chloride of gold and sodium, and a little later Elsner[16] suggested 1 part of chloride of gold and 4 parts potassium chloride dissolved in water and diluted until the solution was of a bright golden-yellow color. A bath[17] made by dissolving equal parts by weight of mercuric and ammonium chlorides in some nitric acid, adding some grain gold, and evaporating to half volume, was intended to be applied hot to the surface of the article without the use of a battery. Neumann[18] studied the character of the deposit formed by electrolysis of gold chloride solutions containing 3 percent of free hydrochloric acid, and found that the addition of 200 gm. of common salt per liter caused a marked improvement in adherence and color.

It is well known that gold is now electrolytically refined in an acid bath of gold chloride, the deposit being of excellent physical properties and a high degree of purity.[19] The essential conditions seem to be a relatively high temperature, addition of hydrochloric acid or a chloride to the bath, and proportioning the current density to suit the other conditions. The warmer the bath the more acid it is, and the purer the anodes the higher the current density allowable. The limiting current density is

[14] Henley, p. 577.

[15] *Loc. cit.*

[16] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, May, 1845; J. Prakt. Chem., **35**, 361 (1845).

[17] Watt and Philipp, p. 167.

[18] Z. Elektrochem., **12**, 575 (1906).

[19] Foerster, p. 277; Electrochem. Met. Ind., **1**, 157; **2**, 26, 213, 221, 261; **4**, 306; **5**, 234; **6**, 114, 355, 408, 450; **8**, 62, 82, 433; Z. Elektrochem., **4**, 379, 402, 421; **9**, 874; D. R. P., 90276, 90511, 207555; Eng. Pat., 6276 (1909); Fr. Pat., 401052 (1909).

that at which chlorine begins to be evolved at the anode. With anodes containing relatively large proportions of silver, asymmetric alternating current can be used to advantage, as it facilitates the separation of the silver chloride from the anode. The solution apparently contains about 30 gm. gold per liter and 3 percent free hydrochloric acid. The temperature varies from 50° to 70° C. in different plants. The current density at the cathode is about 10 amp. per 100 sq. cm., and from 10 to 30 amp. at the anode. The E. M. F. required is about a volt.

The use of a solution of gold bromide has been patented by Spencer.[20] He dissolves as much gold as possible in bromine, or else in a mixture of one part bromine, one part alcohol, two parts acetic acid and eight parts water. A few drops of sulphuric acid is added to the latter solution, and it is electrolyzed as long as necessary with a gold anode to form the bromide. If a heavy plating of gold is to be made, add to each volume of this solution two volumes of ammonium acetate. In the extraction of gold from its ores by the Greenwalt process[21] a solution containing 15 percent common salt and about ⅛ percent bromine as sodium bromide is used for leaching, and the gold electrolytically precipitated as a slimy powder.

Spencer[22] also patented the use of a solution of one part of gold iodide in twenty parts boiling water, to which four parts of a saturated solution of ammonium acetate or chloride were to be added, and the whole boiled a half hour. Parkes[23] patented the use of a molten bath containing 20 ounces of gold iodide and 80 ounces of potassium iodide. The object to be plated was made cathode in this fused bath.

Cyanide Baths.

The advantages of the use of gold baths containing the double cyanide of gold and potassium were early recognized. At that time potassium cyanide was a rare chemical, and expensive; later its price was lowered, but most of that sold was made in such a way that it was much contaminated by impurities. For these

[20] Eng. Pat., Mar. 8, 1841; Repertory of Patent-Inventions, Nov. 1841, 287; Dingler Poly. J., **83**, 378 (1842).

[21] Perkins, Electrochem. Ind., **2**, 24.

[22] *Loc. cit.*

[23] Eng. Pat., Oct. 29, 1844; Repertory of Patent-Inventions, July 1845, 32; Dingler Poly. J., **97**, 294 (1845).

and other reasons many of the earlier workers did not use potassium cyanide in the preparation of their baths, but made the double cyanide of gold and potassium by the interaction of potassium ferrocyanide with some salt of gold. Upon boiling these together the gold displaced part of the iron, which was generally precipitated and filtered off. Those who used potassium cyanide as such adopted several ways of forming the double cyanide. Some were content simply to dissolve gold chloride in the cyanide; some converted the gold to the form of the oxide, cyanide or other compounds before dissolving it in the potassium cyanide, while some used baths consisting mainly of other salts, with only small proportions of cyanide. It is evident that the acid radical originally combined with the gold will remain in the bath in the form of a potassium salt, and these by-products and the proportions of cyanide, gold and water are all that distinguish one bath from another. In order to arrange the mass of recipes for cyanide solutions in any rational manner it is necessary to consider these factors. The material here presented will therefore be taken up in the following order:

A. Baths consisting of a gold salt and potassium cyanide, with or without other salts.

(1) Gold chloride in potassium cyanide.

(2) Gold cyanide in potassium cyanide.

(3) Fulminating gold in potassium cyanide.

(4) Miscellaneous gold salts in potassium cyanide.

(5) Gold salt dissolved in a mixture of potassium cyanide with large proportions of other salts, chiefly phosphates and sulphites.

B. Baths consisting of a gold salt and potassium ferrocyanide, with or without other salts.

These will be followed by the miscellaneous baths containing little or no cyanide, baths intended to produce deposits of a specified color, generally containing added metals, and some general information on the behavior and composition of gold baths.

Gold Chloride in Potassium Cyanide.

The baths made by simply mixing gold chloride and potassium cyanide will be considered in the order of the increase of the ratio of cyanide to gold. A bath which works well at ordinary temperature is said to be made as follows:[24] 3¼ oz. of gold chloride and 3⅛ oz. of potassium cyanide are dissolved in separate portions of water, mixed, and the mixture diluted to one gallon and boiled for half an hour. After cooling it is ready for use. The following[25] appears to be the same bath at a greater dilution: 2 oz. gold (as chloride) and 2 oz. potassium cyanide are dissolved together and diluted to make 12 gallons.

Roseleur is said to recommend the following solution:[26] 10 gm. of gold are converted to chloride, dissolved in 250 c.c. water, and mixed with a solution of 20 gm. of potassium cyanide (98 to 99 percent) in 750 c.c. of water. Spon and Langbein recommend that this be boiled half an hour before use. It is used cold. Langbein states that the cathode current density is 0.12 amp. per 100 sq. cm.; the Chemiker Kalender gives it as 0.2 to 0.25 amp. Langbein states that the bath he gives with the fulminating gold gives a better colored deposit than this one, and that on account of the high content of gold it tends to give reddish deposits unless the current be very carefully regulated.

An early writer[27] recommends a solution of one part of gold chloride and three parts of potassium cyanide in thirty-six parts of water for electroplating, or the same in one hundred and sixteen parts of water for a dipping bath. Hasluck[28] and the Scientific American Cyclopedia[29] copy this bath approximately, but state that it does not give uniform results. Hossauer[30] recommends a similar bath made by dissolving twenty-five parts of gold chloride in sixty to eighty parts of cyanide and three thousand parts water, boiling twenty minutes, adding three thousand parts more water, heating to boiling, cooling and filtering. He

[24] Hasluck, p. 111; Sci. Amer. Cyclopedia, p. 187; practically the same formula in Sci. Am. Supp., 1881, 4937.

[25] Sci. Am., **32**, 405.

[26] Langbein, p. 378; the same formula is given in Chemiker Kalender, **2**, 661, and in English measures in Spon, **I**, 275; Watt and Philipp, p. 181.

[27] Dingler Poly. J., **116**, 246 (1850).

[28] p. 110.

[29] p. 110.

[30] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, 1843; Dingler Poly. J., **90**, 437 (1843).

was the first man, apparently, to recommend the use of the gold anode as a means of keeping the strength of the bath constant. The same bath is given elsewhere[31] in English measures, but with only half as much water.

A bath made by dissolving one part of gold chloride and four parts of potassium cyanide in boiling water is recommended as a dipping bath, the articles being immersed in this for several hours, preferably in contact with a copper wire or a strip of clean zinc.[32]

A paste for gilding articles of zinc[33] is made by dissolving twenty parts of gold chloride and eighty parts of potassium cyanide each in its own weight of water, mixing, filtering, and adding five parts of cream tartar and one hundred parts of powdered chalk. Apply the finished paste with a brush. This appears to be a modification of that patented by Peyraud and Martin,[34] who specified the use of the chloride from ten parts of gold and only sixty parts of cyanide with the same weight of water and other materials as above.

Söhner[35] patented a bath containing one part of gold (as chloride?), ten parts of potassium cyanide (90 percent) and one hundred parts of water, recommending that it be used at 80° to 85° C. This is the same formula elsewhere recommended for use at 100° to 150° F.[36]

The gold in a solution of gold chloride and potassium cyanide can be completely precipitated by low currents, and this has been studied as an electrolytic method for the determination of gold and its separation from some other metals.[37] The solution should be hot (50° to 60°), and the current density at cathode from 0.3 to 0.8 amp. per 100 sq. cm. For 0.1 gm. gold amounts of cyanide varying from 0.75 to 3 gm. have been used. With the use of the rotating anode the current density can be increased to 10 amp. per 100 sq. cm.[38] By proper regulation of the current

[31] Sci. Am. Supp., 1881, 4937.

[32] Henley, p. 576; Spon, **I**, 279.

[33] Henley, p. 580.

[34] Fr. Pat., Feb. 17, 1854; Dingler Poly. J., **134**, 129 (1854).

[35] D. R. P., 35852, July 10, 1885; Dingler Poly. J., **264**, 328 (1887).

[36] Blount, p. 264.

[37] Smith, p. 165; Classen, p. 206; Smith and Muhr, Ber., **24**, 2175; Am. Chem. J., **13**, 417; Smith and Wallace, Ber., **25**, 779; J. Am. Chem. Soc., **17**, 612; Miller, J. Am. Chem. Soc., **26**, 1255.

[38] Withrow, J. Am. Chem. Soc., **28**, 1350; Smith, p. 167.

density, and in some cases addition of other salts, gold can be separated from antimony, cobalt, copper, iron, nickel, palladium, platinum, zinc, molybdenum, tungsten, arsenic and osmium.[39]

The addition of common salt to the bath for plating was recommended in the following formula:[40] The gold chloride from 3.5 gm. gold is dissolved and poured into a solution of 21 gm. cyanide, 21 gm. common salt and 14 gm. crystallized soda in 2 lb. water. A somewhat similar bath was proposed a little later,[41] consisting of a solution in 1½ pints of water of 1 oz. KCN, 60 grains double chloride of gold and sodium and 8 to 10 grains potassium carbonate. The same result is obtained by Ryhiner,[42] who recommends converting the gold to chloride, evaporating to crystallization, neutralizing with sodium carbonate and adding a solution of cyanide until the solution passes through the white milky stage and becomes almost clear. Dilute until the solution contains 3 gm. gold per pound, and boil gently half an hour.

Maximilian Herzog von Leuchtenberg,[43] who owned one of the larger gold-plating establishments of his day, recommended an alkaline bath. One part of gold is converted to chloride, treated with a solution of one part potassium hydroxide, and this mixture added to a solution of two and one-half parts of cyanide and one part potassium hydroxide, and the whole filtered and diluted to the desired volume. He states that the gold is deposited from this bath with a good color, whether diluted very largely (0.0012 gm. gold per 100 c.c.) or fairly concentrated (1.095 gm. per 100 c.c.), so long as the proportion of gold to salts remains as above stated. He recommends, however, that the gold content be between 0.25 and 1.00 gm. per 100 c.c.

Another alkaline bath is recommended by Hessenberg[44] from the practice of Christofle & Co., of Paris. For a very pale yellow deposit he recommends to boil together for two hours 31 gm. gold in the form of chloride, 340 gm. cyanide in solution at 25° Bé. and 18 liters of potassium hydroxide solution (35° Bé.). The less cyanide is used the paler the color. Use cold or hot.

A dipping bath for contact gilding (with a piece of zinc in

[39] Smith, p. 246; Smith and Wallace, *loc. cit.*
[40] Kunst u. Gewerbeblatt f. Bayern, July, 1845; Dingler Poly. J., **97**, 383 (1845).
[41] Sci. Am. [I], **7**, 176 (1852).
[42] Dingler Poly. J., **110**, 423 (1848).
[43] Bull. de. l'Acad. de St. Petersburg, No. 130; Dingler Poly. J., **105**, 341 (1847).
[44] Böttger's Poly. Notizbl., 1847, No. 19; Dingler Poly. J., **106**, 389 (1847).

contact with the work) of somewhat similar composition is recommended by Larsen:[45] Boil together for five minutes 1 dwt. gold (as chloride), 1 quart of water, 8 dwt. potassium cyanide and 4 dwt. of caustic alkali, and then filter.

Gold Cyanide in Potassium Cyanide.

For the purpose, apparently, of avoiding the presence of chlorides in the bath many recipes advocate the conversion of the gold chloride to cyanide. This operation must be conducted with great care to avoid loss, as gold cyanide is very soluble in excess of potassium cyanide. The precipitated cyanide is filtered, washed, and dissolved in a solution of potassium cyanide. Bonney[46] recommends the solution of the precipitate in a "slight excess" of potassium cyanide, and states that the presence of potassium chloride makes the deposit less coherent. Hasluck[47] states that the double cyanide bath is the best, and recommends dissolving the gold cyanide in a strong solution of cyanide and diluting until the solution contains 5 to 15 dwt. gold per gallon. A similar bath[48] containing ½ oz. gold per gallon is intended to work at 130° F. Watt and Philipp[49] recommend solution of the precipitate in a slight excess of a 1 : 8 cyanide solution, and either dilution to a strength of 1½ dwt. gold per quart or evaporation to dryness and solution in hot distilled water to make the same strength. Filter before using, and work at about 130° F. If the baths work slowly add a little more potassium cyanide.

Both Bonney and Hasluck[50] also mention the electrolytic preparation of the double cyanide bath, but the latter author states that the potassium hydroxide formed at the same time is disadvantageous. Elsner[51] dissolved gold leaf in a warm cyanide solution, and used this solution as a hot dipping bath for gilding, mentioning that objects of silver must have a piece of zinc attached to them in order to plate well.

[45] Sci. Am., **66**, 52.
[46] p. 152.
[47] p. 104.
[48] Sci. Am., **33**, 252.
[49] p. 175.
[50] *Loc. cit.*
[51] Berliner Gewerbe-, Industrie- und Handelsblatt, **10**, 67 (1843); Dingler Poly. J., **91**, 307 (1844).

Langbein[52] recommends electrolyzing a cyanide solution, containing 100 gm. per liter, with gold anodes and cathode until it will give a satisfactory deposit, when it should contain about 20 gm. gold per liter. To avoid contamination by the hydroxide, Watt and Philipp[53] recommend separation of the anode and cathode liquids by a porous cup, electrolyzing a solution of cyanide, 1 lb. per gallon, at a temperature of 130° to 150° F., with two Daniell cells, until the bath works well. The gold content may vary from ½ to 2 oz. per gal., but the cyanide should vary in proportion. The Scientific American Cyclopedia[54] gives similar directions, except that a weaker cyanide solution is specified (3 dwt. cyanide per quart).

Wood's solution[55] is made by dissolving 4 oz. (troy) of potassium cyanide and 1 oz. of gold cyanide in a gallon of water. Use at 90° F., with at least two cells.

De Ruolz's solution[56] is made by dissolving ten parts of potassium cyanide in one hundred parts of water, filtering, and dissolving one part of gold cyanide which has been well washed and dried in the dark. The solution is to be kept in a closed vessel in a dark place at 60° to 77° F. for several days, being stirred occasionally. This is about the same proportion as that recommended by Hossauer,[57] who converted one hundred parts of gold to the cyanide and dissolved this in a solution of one thousand two hundred and sixty parts of potassium cyanide.

Grattan[58] states that the addition of potassium sulphocyanide to the bath of gold cyanide dissolved in potassium cyanide makes it possible to use this bath for direct plating of steel.

Neumann[59] studied the precipitation of gold from very dilute solutions of the double cyanide, such as are obtained in the leaching of ores with cyanide, and showed that the current efficiency of the precipitation was considerably under 1 percent. The precipitation of gold from the solutions obtained in leaching ores has been discussed by Walker,[60] who gives a good description

[52] p. 381.
[53] p. 179.
[54] p. 187.
[55] Sci. Am. Cyc., p. 188; Watt and Philipp, p. 177.
[56] Watt and Philipp, p. 180.
[57] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, 1843; Dingler Poly. J., **90**, 437 (1843).
[58] Breslauer Gewerbeblatt, 1861, No. 6; Dingler Poly. J., **160**, 78 (1861).
[59] Z. Elektrochem., **12**, 568 (1906).
[60] Trans. Am. Electrochem. Soc., **4**, 47 (1903).

of the work done up to that time. Most of the papers treat the subject purely from the metallurgical standpoint, and contribute nothing that is of interest along the lines of this review, but Butters[61] states that the solution for electrolysis must be clear, as all solids in it will stick to the electrodes. This probably refers to a migration of the solids to the electrodes under the influence of the current, as has been shown in other cases for colloidal solutions.

Fulminating Gold in Potassium Cyanide.

When ammonia is added to a solution of gold chloride a precipitate of fulminating gold, $Au\begin{bmatrix}(NH_3)_2\\(OH)_2\end{bmatrix}OH$, is formed. This precipitate is easily soluble in potassium cyanide, and the solution, after boiling off the ammonia, is a good plating bath for gold. I have found no statements or experiments to show why it is necessary to boil off the ammonia, but almost all the recipes include this step. Bonney[62] states that the fulminate bath, while good when new, is likely to yield a dark deposit when old. The fulminating gold precipitate is explosive when dry; it should be washed carefully and then dissolved as soon as possible in the cyanide.

Watt and Philipp[63] recommend dissolving the fulminating gold from 1½ dwt. of the metal in a strong solution of cyanide, filtering, and diluting to a quart. Namais[64] recommends dissolving fulminating gold in a 1 percent solution of cyanide and boiling. One gm. of gold per liter is the minimum quantity that should be used.

Roseleur's solution[65] is made by dissolving the fulminating gold from ten parts of metal in thirty parts of cyanide (70 percent) dissolved in one thousand parts of water, and boiling an hour to drive off the ammonia. This is almost identical with the formula of Langbein,[66] who dissolves the fulminating gold from 3.5 gm. of the metal in 1 liter water containing 10 to 15 gm.

[61] Proc. Chem. Met. Soc. S. Africa, **2**; Electrochem. Ind., **2**, 53.

[62] p. 152.

[63] p. 176.

[64] Monit. Sci., **18**, 487.

[65] Watt and Philipp, p. 180; Hasluck, p. 111; the same formula transposed into English weights appears in Spon, **I**, 275.

[66] p. 377, also in Foerster, p. 254.

of cyanide (98 to 99 percent). He states that with the electrodes 10 cm. apart the voltage with the bath containing 10 gm. cyanide is 1.35; with 15 gm. cyanide it is 1.2. Current density 0.15 amp. per 100 sq. cm. After dissolving the gold the solution is boiled until all the ammonia is gone, the water lost is replaced, and the solution is filtered. Too great an excess of cyanide gives the deposit a pale color. The stronger the current the less excess of cyanide is required. The bath can be used diluted with its own volume of water, which is, of course, cheaper, but the voltage is higher (2 volts). Current density as above.

C. H. P.[67] recommends a solution of ½ oz. gold (in the form of fulminating gold) in 1 oz. cyanide and 1 qt. water for plating the inside of thimbles. On another occasion[68] he modifies this bath as follows: Water 1 gal., cyanide ½ to 2 oz., sodium phosphate 1 oz., gold (as fulminating gold) ½ oz. On another occasion[69] he gives another modification: Water 1 gal., cyanide 1½ to 2 oz., sodium acid sulphite ¼ oz., gold (as fulminating gold) ½ oz. This formula is for gilding the caps to perfume bottles.

Elsner[70] converted the gold to chloride, added 0.3 of its weight of common salt, evaporated to dryness, diluted, precipitated with excess of ammonia, filtered, washed, and dissolved in a slight excess of cyanide solution. Dilute until there are 2 lbs. water per 14 gm. gold. Use warm. A little later he recommended a modified form of this bath: 3.5 gm. gold is converted to fulminating gold, washed, and dissolved in a solution of 10.5 gm. cyanide in ½ lb. water, boiled twenty minutes, replacing water lost by evaporation, and a solution of 3.5 gm. cyanide and 7 gm. potassium hydroxide in a little water added. Filter if necessary.

A solution containing a larger proportion of cyanide is recommended by Langbein[71] for the hot process: 1 gm. of gold is converted to fulminating gold and washed. It is dissolved in a solution of 5 gm. of 98 percent cyanide in a liter of water. Voltage 1.0 when electrodes are 10 cm. apart. Current density 0.1 amp. per 100 sq. cm. Work at 70° to 75° C. All ammonia is to be boiled off before use, as usual.

[67] Met. Ind., **10**, 428.
[68] Met. Ind., **10**, 428.
[69] Met. Ind., **10**, 340.
[70] Dingler Poly. J., **112**, 66 (1849).
[71] p. 380.

A still larger proportion of cyanide is recommended for use in a dipping bath[72] ascribed to Dr. Ebermayer: 10 gm. of gold is converted to fulminating gold and dissolved in a saturated solution of 100 gm. of cyanide. This solution is then diluted to 1 liter. It is to be used hot.

Miscellaneous Cyanide Baths.

A solution of gold oxide in potassium cyanide has been recommended as a plating bath. General directions[73] call for the solution of the gold as chloride, its precipitation as oxide by an excess of magnesia, filtration and washing. The precipitate is then digested in dilute nitric acid to remove excess of magnesia, washed, and dissolved in potassium cyanide. Specific directions were given for the preparation of this bath in the patent of the Elkingtons[74] in 1840. They recommended the solution of 2 oz. of gold oxide in 2 lb. of potassium or sodium cyanide dissolved in 10 lb. of water and boiling this solution for half an hour. Dipping in the boiling solution is said to produce a thin coat of gold, but a thicker coat is obtained by electrolysis in the cold solution. The gold content of the bath must be maintained. Kemp[75] converted one part of gold to oxide, and dissolved it in a solution of eight parts of cyanide in eighty parts of boiling water. A later writer[76] recommended a bath containing ½ oz. of gold oxide and 14 to 16 oz. of potassium cyanide per gallon of water. This bath was to be used hot—at about 130° F. on copper objects, and 200° F. on silver ones.

Spencer[77] recommended the solution of one part of gold iodide in a solution of two parts of potassium cyanide and ten parts of water. This solution is then to be boiled for a time, replacing the water lost by evaporation.

Watt's gilding solution[78] is made by dissolving the chloride from 1½ dwt. of gold and precipitating it with ammonium sulphide. The precipitate is washed by decantation, dissolved in

[72] Spon, **1**, 282.

[73] Sci. Am., **32**, 218.

[74] Eng. Pat. of G. R. Elkington and H. Elkington, Mar. 25, 1840; London J. Arts, Sept. 1841, 83; Dingler Poly. J., **82**, 124, 380 (1841).

[75] Chem. Gazette, March, 1847, No. 106; Dingler Poly. J., **104**, 315 (1847).

[76] Sci. Am. Supp. **7**, 2540 (1879).

[77] Eng. Pat. Mar. 8, 1841; Repertory of Patent-Inventions, Nov. 1841, 287; Dingler Poly. J., **83**, 378 (1842).

[78] Watt and Philipp, p. 184.

a moderate excess of strong potassium cyanide, and diluted to make one quart. It should be worked at about 130° F. This bath is highly recommended, and it is stated that articles do not require "quicking" in a mercury solution before plating in it, as is the case with some other solutions.

Cyanide Baths with Large Amounts of Other Salts.

Many baths have been proposed which contain large quantities of phosphates and sulphites. Those which contain relatively large quantities of cyanide will be considered here; those where the cyanide is present in only a small quantity will be considered under a later head (page 49). Sodium bisulphite appears to be useful in the baths to improve the color of the deposit. C. H. P.[79] recommends that if a gold bath plates dull and hard it be boiled and ½ oz. sodium acid sulphite per gallon added, and states that this property of improving bad baths is characteristic of the sulphite. O. A. Hillman[80] states that the presence of the bisulphite gives gold a light canary color, so that it gives the proper tone on copper articles.

C. H. P.[81] states that Roseleur's solution is the best for light-colored gold, and gives the following formula for it: Water 1 gal., sodium phosphate 8 oz., sodium bisulphite 1 oz., potassium cyanide 2½ dwt., gold 2½ dwt. The bath is to be used at 130° to 160° F., with a platinum anode. A little later, under the head of a "22-karat gold solution,"[82] he gives the same solution, except that the bisulphite is increased to 1¼ oz., and it is specified that the gold is to be used in form of the chloride, which is probably true also for the other formula. For yellow gilding on steel chains he recommends flashing in a warm bright brass solution and plating in a solution which is Roseleur's solution with the cyanide and gold each increased to 6 dwt. per gal.[83] This solution is to be worked at a little higher temperature (160° to 180° F.). A similar solution is given by the same author for "yellow gold solution"[84] and for "Grecian or Roman finish

[79] Met. Ind., 10, 512.
[80] Met. Ind., 8, 29.
[81] Met. Ind., 8, 222.
[82] Met. Ind., 8, 392.
[83] Met. Ind., 9, 437.
[84] Met. Ind., 9, 479.

gold,"[85] as follows: Water 1 gal., sodium phosphate 6 oz., sodium bisulphite 1 oz., potassium cyanide 6 dwt., neutral gold chloride 7½ dwt. This is to be used with a 22-karat anode.

For "dead lustre gold" the article is to be given successive coats of copper and silver, and then plated in a hot solution containing 2⅕ gal. water, 21 oz. sodium phosphate, 3½ oz. sodium bisulphite, ⅓ oz. potassium cyanide and ⅔ oz. gold chloride. Use a strong current and a platinum anode.[86] The same formula appears in another handbook[87] except that, perhaps through an error, the bisulphate is specified instead of the bisulphite. The solution is to be used warm (120° to 180° F.) according to the latter authority.

Another recipe[88] calls for 60 gm. sodium phosphate, 10 gm. sodium sulphite, 2 gm. potassium cyanide and 2 gm. gold chloride per liter. It is to be electrolyzed at 50° C. The same formula with the cyanide increased to 5 gm. is recommended elsewhere[89] for gilding by dipping, the object being kept in contact with a piece of zinc. This is also to be done in hot solution.

A bath much richer in phosphate is as follows:[90] 50 gm. sodium phosphate, 15 gm. cryst. sodium sulphite, 1 gm. potassium cyanide and 1.5 gm. gold chloride per liter water. The proper current density is ⅕ to ¼ amp. per 100 sq. cm.

A brass-gilding bath is recommended as follows:[91] Dissolve five parts of sodium phosphate and three parts of potassium hydroxide in seven hundred and fifty parts water, and one part of gold chloride and sixteen parts of potassium cyanide in two hundred and fifty parts of water. Mix and boil. This is recommended for a hot dipping bath. The same bath is also recommended as a plating bath.[92]

O. A. H.[93] recommends an electrolytically prepared bath. Six oz. of cyanide and 3 oz. of sodium phosphate are dissolved in a gallon of water, and 30 dwt. of gold from a gold anode dissolved in this by electrolysis.

[85] Met. Ind., **10**, 322.
[86] Spon, **I**, 286.
[87] Sci. Am. Cyc., p. 188.
[88] Erfind. u. Erf., **32**, 401; Z. Elektrochem., **12**, 93 (1906).
[89] Henley, p. 580.
[90] Chem. Kalender, **2**, 661 (1913).
[91] Henley, p. 576.
[92] Elektrochem. Z., **16**, 186; C. A., **4**, 150 (1910).
[93] Met. Ind., **9**, 313.

Ferrocyanide Baths.

In the early days of electroplating, potassium ferrocyanide was cheap and reasonably pure, whereas the cyanide was both expensive and impure. Many workers therefore used the ferrocyanide as the basis of the bath. When the ferrocyanide is boiled with a gold salt a double cyanide of gold and potassium is formed, and a precipitate of either ferric hydroxide or prussian blue is formed, depending on whether or not alkali is added to the bath. The reactions have been worked out and are given by Beutel (Z. angew. Chem. **25**, 995 (1912)) as follows:

$$28HAuCl_4 + 35K_4Fe(CN)_6 + 10O =$$
$$28KAu(CN)_4 + 112KCl + 8HCN + 5Fe_7(CN)_{18} + 10H_2O$$

When an alkali is added:

$$14HAuCl_4 + 14K_4Fe(CN)_6 + 13K_2CO_3 + 7O + 10H_2O =$$
$$14KAu(CN)_4 + 56KCl + 4HCN + 10Fe(OH)_3 + 4K_3Fe(CN)_6$$
$$+ 13CO_2$$

With less ferrocyanide:

$$14HAuCl_4 + 10K_4Fe(CN)_6 + 15K_2CO_3 + 5O + 10H_2O =$$
$$14KAu(CN)_4 + 56KCl + 4HCN + 15CO_2 + 10Fe(OH)_3$$

The same author has assembled a number of recipes for ferrocyanide baths, which he has recalculated on the basis of grams per liter. Besides the formulas of Frankenstein, Briant and Langbein, which I have included in their original form in this article, he gives the following from sources not accessible to me: Elkington's bath[94] contained 7.81 gm. gold as chloride or cyanide, and 125 gm. of "prussiate de potasse" which is probably ferrocyanide. Kaiser and Alexander[95] use 10 gm. gold chloride and 100 gm. ferrocyanide. Elsner[96] gives what is evidently a modification of his ferrocyanide bath, described later, containing 3 gm. gold chloride, 116 gm. ferrocyanide and 15 gm. crystallized soda per liter. Stockmeyer[97] uses 1.5 to 2 gm. gold in the form of chloride or fulminating gold, 15 to 20 gm. ferrocyanide and 10

[94] Compt. rend., **13**, 998.
[95] Bayerisches Kunst- und Gewerbeblatt, 1842, Heft 4.
[96] Die galvanische Vergoldung und Versilberung, 2 Aufl. 1851, Leipzig, F. Amelang.
[97] Handbuch der Galvanostegie und Galvanoplastik. Halle a|S., 1899, Knapp.

to 12 gm. potassium carbonate. Pfanhauser[98] uses 2.65 gm. gold chloride, 15 gm. ferrocyanide and 15 gm. potassium carbonate. Taucher[99] uses 1.5 gm. gold chloride, 20 gm. ferrocyanide, 15 gm. potassium carbonate and 30 gm. ammonium chloride. Beutel himself recommends as a normal bath a solution of 13.8 gm. potassium carbonate and 21.2 gm. ferrocyanide per liter, *i. e.*, a solution N/10 with respect to the carbonate and N/20 with respect to the ferrocyanide, adding about 0.5 gm. gold as chloride.

The principal disadvantage of the ferrocyanide bath appears to be that it does not dissolve the gold anode readily, and the gold content of the solution must be maintained by the addition of gold chloride and oxide.[100] The same authors state that the color of the deposit from the ferrocyanide bath is richer than that from the cyanide bath, and the same statement is made by Bagaration.[101] The bath is more stable than the cyanide bath,[102] and there is said to be less danger of poisoning the workers. It is evident that the action of the air on the bath would give very little hydrocyanic acid as compared to a cyanide bath; and the poisoning by absorption through the pores of the skin of the hands, and through cuts, scratches, etc., which is said to be frequently observed with cyanide baths, would probably be reduced to a minimum with this bath, as the ferrocyanide is itself not poisonous.

Von Ruolz,[103] in his French patent of December 19, 1840, included solutions of gold cyanide or chloride in either potassium ferrocyanide or ferricyanide. Bagaration[104] recommends the solution of metallic gold by long boiling in a solution of potassium ferrocyanide. Most recipes, however, use the gold in the form of the chloride or oxide.

Bacquerel[105] mentions the use of a solution containing 1 gm. dry gold chloride, 10 gm. ferrocyanide and 200 c.c. water, and states that organic substances in solution tend to reduce the gold to the metallic state. He evidently considered that the above

[98] Elektroplattierung, Wien, 1900, Spielhagen und Schurich.

[99] Handbuch der Galvanoplastik, Frankfurt, 1900, Keller.

[100] Zinin, Dingler Poly. J., **259**, 26 (1886); L. Elsner, J. Prakt. Chem., **35**, 361 (1845).

[101] Bull. de l'Acad. imp. des Scienc. de St. Petersb. **2**, 136 (1843); Dingler Poly. J., **92**, 206 (1844).

[102] Elsner, *loc. cit.*

[103] Dumas, Compt. rend., 1841, No. 22 (Nov.); Dingler Poly. J., **83**, 125 (1842).

[104] *Loc. cit.*

[105] Compt. rend., 1842, 1st. semester, No. 4; Dingler Poly. J., **84**, 33 (1842).

solution contained too little ferrocyanide, for he states that he prefers a solution made by dissolving 1 gm. of dry gold chloride and 10 gm. ferrocyanide in 100 c.c. of water and diluting with 100 c.c. of saturated ferrocyanide solution. This solution can then be diluted with one or two volumes of water if desired, as this dilution improves the tone and causes the deposit to be less matte. This formula is copied by Watt and Philipp;[106] and Fehling,[107] after trying the process of von Ruolz, recommended a solution which is practically identical with it. His solution was made by dissolving the chloride from 3.5 gm. gold with 35 gm. ferrocyanide in 1½ lb. water, and either boiling or heating in a bath of boiling water until the prussian blue separates and can be easily removed by decantation. He states that prussian blue is formed at the anode when this solution is used. He preferred the cyanide solution to the ferrocyanide, but considered the former very expensive. He recommends the substitution of 21 gm. of the crude cyanide for the ferrocyanide in the above formula. He states that the ferrocyanide maintains the quality of the deposit after considerable use much better than the cyanide. For plating brass, zinc and tin he recommends the use of a solution containing 28 gm. ferrocyanide, 7 to 10 gm. cyanide, water 1½ to 2 lb., and the chloride from 3.5 gm. gold. This solution is to be used cold.

Watt and Philipp[108] dissolve 200 gm. ferrocyanide and 500 gm. salammoniac in about 4 liters of water and heat to boiling. The chloride from 100 gm. gold is dissolved in a liter of water, and 200 c.c. of this solution is added a little at a time to the boiling ferrocyanide solution, oxide of iron being precipitated(?). The solution is then cooled, filtered and made up to 5 liters. To increase the conductivity a small quantity of potassium cyanide may be added, but not enough so that hydrocyanic acid fumes are evolved on boiling. The bath is to be used at 100° to 150° F. When it ceases to work well it may be strengthened by adding 200 c.c. more of the gold solution, proceeding as above.

To avoid the formation of prussian blue in the bath various authors have recommended the addition of alkalies to it. Ebermayer[109] converted 100 gm. gold to chloride and dissolved it in

[106] p. 176.
[107] Dingler Poly. J., **86**, 350 (1842).
[108] p. 183.
[109] Dingler Poly. J., **224**, 631 (1877).

a liter of water. A solution of 300 gm. potassium ferrocyanide, 100 gm. potassium carbonate and 50 gm. salammoniac in 4 liters of water is warmed to 30° or 40° (C. ?), 200 c.c. of the above solution added, and the whole boiled for twenty to thirty minutes, cooled, filtered and diluted to 5 liters. Small quantities of KCN may be added from time to time to improve the conductivity of the bath, and when it is impoverished 200 c.c. of the gold chloride solution may be added as before. This is evidently the same solution as that recommended by Watt and Philipp, except that part of the salammoniac has been replaced by potassium carbonate. This solution of Ebermayer's has been copied by several writers[110] after conversion to English weights and measures.

Another somewhat similar bath[111] contains 7 oz. ferrocyanide, 5 oz. potassium carbonate, 1 oz. salammoniac, 1 oz. gold (as chloride) and 2⅕ gal. water. The directions state that all the constituents except the gold chloride are to be boiled together and filtered, and then the gold chloride added.

Roseleur is credited with recommending the following bath:[112] twenty parts of ferrocyanide, thirty parts of potassium carbonate and three parts of salammoniac are boiled together in one thousand parts of water and filtered. Fifteen parts of gold chloride are now dissolved in a little water and added to the liquor. Fulminating gold may be used in place of the chloride, and small quantities of hydrocyanic acid may be added to the bath to make the deposit brighter, but this makes the bath work more slowly. The bath is to be used cold. Watt and Philipp[113] state that the deposit of gold from cold solutions varies greatly in color. With a good bath and sufficient current density the color will be a pure yellow. Sometimes the deposit is several shades lighter, and sometimes it is earthy gray. There should be about twice as much cyanide (ferrocyanide?) in the bath as gold; if the gold is in excess the deposit will be blackish or dark red. If cyanide is in excess the operation is slow and the coating is a dull gray, and sometimes partly or wholly redissolves in the bath. A low voltage is to be used. (One Daniell cell.)

[110] Spon, **I**, 279; Sci. Am. Supp., 1881, 4937; Sci. Am. Cyc., p. 187.
[111] Spon, **I**, 275.
[112] Watt and Philipp, p. 181; Sci. Am. Cyc., p. 188.
[113] *Loc. cit.*

Elsner[114] recommended a solution containing 10.5 gm. gold (as chloride), 168 gm. ferrocyanide and 1½ quarts of water, to which he adds a solution of 56 to 70 gm. of crystallized soda in a little water. He states that for plating large objects this bath may be diluted to 6 quarts. He later[115] modifies this bath, recommending the conversion of one part of dry chloride of gold to fulminating gold, and its solution in two parts of ferrocyanide dissolved in twelve parts of water. Boil this mixture and filter. An alternative method is to dissolve two parts of ferrocyanide and one and one-half parts of soda in twelve parts of boiling water, and add the chloride of gold (one part) directly to this. This is stated to be just as good as the fulminating bath. He also states that the addition of sodium chloride to a ferrocyanide bath intended for *contact* gilding is advantageous.

Söhner[116] recommends the use at 40° to 45° C. of a bath containing 50 gm. gold, 400 gm. sodium bicarbonate, 700 gm. potassium ferrocyanide and 50 liters of water.

Gräger,[117] referring to the baths calling for the use of alkalies and gold chloride with potassium ferrocyanide, states that an excess of alkali must not be used or the deposit will be likely to be dark and non-adherent. He recommends that such solutions should be made distinctly acid with sulphuric acid before use.

Langbein[118] gives the following bath for use cold: Potassium ferrocyanide 15 gm., sodium carbonate (dry) 15 gm., gold (in the form of chloride or fulminating gold) 2 gm., water 1 liter. The solution of the carbonate and ferrocyanide is heated to boiling, the gold chloride added, and boiling continued for fifteen minutes. If the fulminating gold be used, the boiling must be continued until there is no more odor of ammonia. Cool, replace the water lost by evaporation, and filter. This bath is said to give a good coat on all metals, even steel and iron, without first coating with copper. The same bath is also given by others.[119]

The addition of common salt was the principal novelty in

[114] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, 1842; Dingler Poly. J., **88**, 30 (1843).

[115] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, May, 1845; J. Prakt. Chem., **35**, 361 (1845).

[116] D. R. P., 35852, July 10, 1885; Dingler Poly. J., **264**, 328 (1887).

[117] J. Prakt. Chem., **30**, 343 (1843); Dingler Poly, J., **90**, 446 (1843).

[118] p. 379.

[119] Van Horne, p. 141; Erfind. u. Erfahr., **32**, 401, abstr. in Z. Elektrochem., **12**, 93 (1906).

Frankenstein's contact process of gilding.[120] He used a solution of one part of gold chloride and ten parts each of potassium ferrocyanide and common salt in fifty parts of water. The ferrocyanide can be partly replaced by carbonate, the following formula being also recommended: Gold chloride one part, ferrocyanide six parts, potassium carbonate four parts, common salt six parts, water fifty parts. The object to be plated was immersed in the bath in contact with a piece of zinc. The process is carried out in a hot bath. Fehling tried out the principle of Frankenstein's process, by adding common salt to dipping baths of gold chloride in ferrocyanide and cyanide which he was using, and found that it worked well. (See also statement of Elsner, above.)

The use of common salt is also recommended in a dipping bath given by Henley,[121] for use cold: Seven parts of gold chloride, thirty parts of ferrocyanide, thirty parts of potassium hydroxide and thirty parts of common salt are dissolved in one thousand parts of water. The object to be coated is placed in contact with a piece of zinc.

Selmi[122] boils together 1 gm. soda, 1 gm. ferrocyanide and 30 c.c. water, adds the fulminating gold from 0.5 gm. gold, boils off all the ammonia, replacing water lost, and filters. Wash until total volume is 65 c.c. Use a Daniell cell, with such a weak current that the gold can not be seen on the cathode for fifteen minutes. Plate fifteen to sixteen hours. Too strong a current gives a brown tone. The addition of some salammoniac with the gold is advantageous, and common salt to the extent of a 1:8 solution did not seem to be injurious. More salt gave the gold a brown color. The presence of organic substances in the potassium carbonate may cause reduction of the solution and the formation of gold spangles. Adding the fulminating gold in small portions and boiling off most of the ammonia after each addition seemed to prevent the reduction, as did also the increase of the ferrocyanide to three parts.

Jacobi[123] states that the following process of Briant gives

[120] Fehling, Dingler Poly. J., **87**, 290 (1843).

[121] p. 580.

[122] Manuel de dorure et d'argenture electrochimique par simple immersion. M. J. Selmi. Translated from the Italian and enlarged by M. E. de Valicourt, Paris, 1845, **1**, 18; Technologiste, Aug., 1845, 526; Dingler Poly. J., **98**, 27 (1845).

[123] Bull. de St. Petersb. T. I., No. 5; Dingler Poly. J., **87**, 283 (1843).

better results than the process of Ruolz: The gold oxide made from 36 gm. gold is boiled twenty minutes in a solution of 1 lb. ferrocyanide and 112 gm. potassium hydroxide in 10 lb. water and filtered. Only one cell of a battery is to be used for plating to get the best results. The bath can be worked hot or cold, but it is safer to use it cold. The same formula is given by others[124] except that the amount of gold is stated as 34 gm. Elsner[125] tried this, and recommends the following modification: Convert 7 gm. gold to oxide, boil with a solution of ½ lb. ferrocyanide and 14 gm. potassium hydroxide for five minutes, filter. This bath is said to give a fine matte deposit. Later Briant seems to have modified this formula by increasing the amount of gold.[126] He dissolved the oxide from 52 gm. gold in a solution of 500 gm. ferrocyanide and 120 gm. potassium hydroxide in 5 liters of water, and boils the mixture twenty minutes, cools and filters. The solution may be used hot or cold.

Kendall[127] patents a bath for gold plating, consisting of a combination of an aurate and a ferrocyanide, such as potassium aurate with a small excess of potassium hydroxide and a large excess of potassium ferrocyanide.

Hessenberg[128] gives the following as the recipe of Christofle & Co., Paris, successors to Elkington and Ruolz: Convert 31 gm. gold to chloride, and add 1,960 gm. potassium cyanide in the form of a solution of 25° Bé., and 840 gm. potassium hydroxide in the form of a solution of 25° Bé., and 36 liters of ferrocyanide solution at 30° Bé. Boil the whole two hours, when it should have the gravity of 35° Bé. In the meantime the following solution is prepared: 150 gm. gold are converted to chloride, 9,000 gm. potassium bicarbonate and 30 kg. water are taken. Half of the bicarbonate is dissolved in most of the water, and the solution heated. The gold chloride is dissolved in the rest of the water, and the other half of the bicarbonate added to it in small portions. This is then added to the solution of the rest of the bicarbonate, and the whole boiled two hours. This second solution is then added to the first, and the bath is ready. It

[124] Watt and Philipp, p. 177; Sci. Am. Cyc., p. 188.

[125] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, 1843; Dingler Poly. J., **89**, 22 (1843).

[126] Dingler Poly. J., **136**, 58 (1855).

[127] U. S. Pat., 724107 (1903).

[128] Böttger's Poly. Notizbl., 1847, No. 19; Dingler Poly. J., **106**, 389 (1847).

should be used at 30° to 35° C., with a gold anode. Every evening as much gold (in the form of the chloride) should be added as has been precipitated during the day. After a month of use, add cyanide every two days in the proportion of 62 gm. per each 20 kg. of work gilded.

Mongeot[129] patents a solution containing sodium pyrophosphate and potassium ferrocyanide 1 kg. each, and 10 gm. gold. Boil these together in solution (amount of water not stated) for three days, and use as a dipping bath. Dip two minutes, rinse, and dip in cyanide solution containing 2 gm. gold and 20 gm. potassium cyanide per liter, to make the gold adhere well, then repeat dipping in first bath until the proper color is obtained.

Miscellaneous Baths Containing Little or No Cyanide.

The use of phosphate solutions seems to have been introduced by Roseleur and Lanaux[130] in order to prevent the poisoning of the workers by cyanide. They state that the use of either sulphite or phosphate solutions alone does not produce a good deposit, but the mixture of both does well. They also state that a solution of gold chloride in sodium pyrophosphate will gild by immersion, while a solution in ordinary phosphate will not do so. They state that it does not matter whether these baths are acid or alkaline. Spon[131] recommends the use of a pyrophosphate solution to which a few drops of sulphurous or hydrocyanic acid are added as a dipping bath for gilding articles of silver.

The formula of Roseleur is given in a number of varying forms, all giving the same solution.[132] Langbein's version is: Sodium phosphate, cryst., 60 gm.; sodium sulphite, cryst., 10 gm.; potassium cyanide (98 to 99 percent) 2 gm.; gold (as chloride) 1 gm.; water 1 liter. Voltage 1.5 when electrodes are 10 cm. apart. Current density 0.12 amp. per 100 sq. cm. If this is to be used for the direct gilding of steel, only 1 gram of cyanide is to be used. Langbein recommends increasing the sulphite to 15 or 20 gm. To prepare the solution dissolve the sulphite and phosphate in warm water, cool completely, dissolve the cyanide,

[129] Fr. Pat., April 6, 1854; Dingler Poly. J., **134**, 132 (1854).

[130] Technologiste, May, 1847, 341; Dingler Poly. J., **105**, 29 (1847).

[131] **I**, 288.

[132] Langbein, p. 380; Spon, **I**, 279; Watt and Philipp, p. 177; Hasluck, p. 110; Sci. Am. Supp., 1881, 4936.

and add the gold as a solution. Work at 70° to 75° C. The recipe given by Watt and Philipp calls for the acid sulphite instead of the normal salt, and the cyanide is reduced to 1 gm. They also give a modification of the same formula: Fifty parts of sodium phosphate, twelve and one-half parts of sodium bisulphite, one-half part of potassium cyanide and one part of gold (as chloride) to every one thousand parts of water. They recommend dissolving the phosphate in eight hundred parts of hot water, cooling and filtering, then dissolving the gold chloride in one hundred parts of water and the bisulphite and cyanide in the other one hundred parts. Pour the gold solution into the phosphate solution, with stirring, and then add the other solution promptly. The modification is stated to be for the purpose of making the bath suitable for gilding steel or wrought iron directly. Work at 122° to 176° F. (50° to 80° C.). Watt and Philipp ascribe this modified formula also to Roseleur. The same formula in English weights is given by others.[133]

Another very similar solution is recommended by several authors[134] for use on brass and bronze. It contains 1½ oz. sodium bisulphite, 6½ oz. sodium phosphate, ¾ oz. potassium bicarbonate, ¾ oz. sodium hydroxide, ¼ oz. potassium cyanide and ½ oz. gold chloride per gallon of water. All except the gold salt are dissolved together in hot water, cooled, and the gold added as a solution. Work at 130° F.

A pyrophosphate solution, also attributed to Roseleur, is given by several authors.[135] Eight hundred gm. sodium pyrophosphate is dissolved in 10 liters of water, filtered, 20 gm. gold converted to chloride and dissolved is added to this, then 8 gm. of 12 percent hydrocyanic acid is added, with stirring, and the solution heated to boiling. Too little hydrocyanic acid will give the solution a wine color; it should be colorless when hot, and yellow when cold. An excess of hydrocyanic acid retards the deposition of the gold. The articles should be agitated in the bath, which is used as a dip, without a battery.

Another pyrophosphate formula is given by Delatot,[136] who

[133] Spon, **I**, 279; Sci. Am. Cyc., p. 186; Hasluck, p. 110; Sci. Am. Supp., 1881, 4937.

[134] Hasluck, p. 110; Sci. Am. Cyc., p. 186; Sci. Am. Supp., 4937.

[135] Watt and Philipp, p. 168; Sci. Am. Cyc., p. 188; Henley, p. 576; Spon, **I**, 279; Sci. Am. **44**, 74 (1881).

[136] Eng. Pat., Oct. 14, 1873; Dingler Poly. J., **215**, 471 (1875).

patents the following: Water 100 lb., sodium bicarbonate 4½ lb., sodium pyrophosphate 1½ lb., gold chloride ¼ oz., hydrocyanic acid 2 drops and sodium cyanide 1 oz.

Elsner[137] states that a deposit of gold can be obtained from a solution of fulminating gold in sodium sulphite, made strongly alkaline with soda, but that it is of a light brownish color. He obtained similar results with sodium thiosulphate.

Woolrich[138] recommended converting 3 oz. fine gold to oxide and dissolving it in a solution of sodium sulphite made by saturating with sulphur dioxide a solution of 28 lb. sodium carbonate in 44 lb. water. One-fifth more of this solution is used than is necessary to dissolve the gold oxide. The solution is allowed to stand twenty-four hours, and filtered.

Fizeau[139] recommends a solution of 1 gm. gold and 4 gm. sodium thiosulphate in a liter of water.

For plating articles of aluminum it is recommended[140] to dissolve six parts of gold, precipitate with thirty parts slaked lime, and dissolve the precipitate in a warm solution of twenty parts of sodium thiosulphate in one thousand parts of water. The same author recommends another bath for the same purpose: Twenty parts of gold, dissolved, twenty parts of sodium sulphate (?), six hundred and sixty parts of sodium phosphate and forty parts of potassium cyanide dissolved in one thousand parts of water.

Tissier[141] recommends another thiosulphate bath for plating aluminum: Eight grams of gold is dissolved and precipitated with the minimum amount of lime. The precipitate is digested with a warm solution of 20 gm. hypo per liter of water. Use as a dip.

Poole[142] patented a solution made by dissolving the fulminating gold obtained from an ounce of metal in a gallon of water containing 8 oz. of sodium thiosulphate or the equivalent amount of potassium thiosulphate and boiling an hour. Electrolyze at 30° to 52° R.

[137] J. Prakt. Chem., **35**, 361 (1845); from Ver. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, May, 1845.

[138] Mechanics Mag., Feb. 1843, 146; Dingler Poly. J., **88**, 48 (1843).

[139] Watt and Philipp, p. 177; Sci. Am. Cyc., p. 188.

[140] Henley, p. 576.

[141] Compt. rend., July, 1859, No. 1; Dingler Poly. J., **153**, 195 (1859).

[142] Eng. Pat., May 25, 1843; London J. Arts, Feb. 1844, 14; Dingler Poly. J., **91**, 482 (1844).

Levol[143] recommends as a dipping bath for gilding silver a solution of gold chloride to which has been added enough potassium sulphocyanide to redissolve the precipitate at first formed. This solution is to be made acid with hydrochloric acid, and used boiling hot, without a battery. Elsner[144] tried the above bath, and found that the color of the deposit was a blackish yellow instead of a pure yellow.

Perkin and Prebble[145] state that gold may be deposited very satisfactorily from solutions of its salts in ammonium sulphocyanide. With a current density of 0.2 amp. per 100 sq. cm. the deposition of 0.05 to 0.08 gm. was complete in five to six hours. Temperature recommended, 30° to 40° C.

Before the art of electroplating was known G. R. Elkington discovered a process of dipping brass and other objects in a solution containing gold and thereby depositing the gold upon them. As already pointed out, this is in reality an electrolytic process, in which part of the object to be plated is dissolved to produce the current necessary to deposit the gold. His process[146] consisted in dissolving 5 oz. (troy) of gold in 21 oz. (av.) of nitric acid (sp. g. 1.45), 17 oz. of hydrochloric acid (sp. g. 1.15) and 14 oz. water. This was warmed until free from fumes, decanted from the residue of silver chloride, a solution of 20 lb. of potassium acid carbonate in 4 gal. of water was added, and the whole boiled gently for two hours. The objects to be plated were hung in this bath until they attained the desired shade. Watt and Philipp state that articles of silver or German silver must have a piece of zinc attached to them.

Dr. Schubarth[147] tried out the method, and stated that a good deal of gold oxide was precipitated during the boiling, and that the water lost by evaporation must be replaced. He criticized the formula for the bath on the ground that the large amount of potassium nitrate in the bath decreases the solubility of the gold and that much of the potassium bicarbonate was wasted. He recommended that the gold chloride be evaporated until as near neutral as possible, made into a 1 : 130 solution, and the

[143] J. de Pharmacie, Mar., 1843, 213; Dingler Poly. J., **88**, 364 (1843).

[144] Dingler Poly. J., **90**, 311 (1843).

[145] J. Chem. Soc., **86**, 370.

[146] London J. Arts, May, 1837, 99; Dingler Poly. J., **65**, 42 (1837).

[147] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, 1837, 152; Dingler Poly. J., **66**, 126 (1837); J. Prakt. Chem., **11**, 339 (1837).

potassium bicarbonate added in small portions until the solution began to be greenish and a little cloudy. About seven parts of the bicarbonate would be required for one part of gold. He states that the presence of potassium chloride increases the solubility of the gold, and that sodium bicarbonate may be used in place of the potassium salt if 50 percent more of it be used.

It is stated[148] that the purpose of the long boiling in the preparation of Elkington's solution is the reduction of the gold to the monovalent state, and that Elkington found that the rate of this reduction and the success of the preparation depended on the quality of the carbonate. The author stated that this was due to the organic impurities in the carbonate.

Another similar solution[149] was made by dissolving the chloride from 6¼ dwt. of gold in a quart of water, adding 1 lb. potassium bicarbonate and boiling two hours. This is also to be used warm as a dip.

A similar solution with sodium carbonate is made[150] by dissolving six parts of gold chloride and twenty-two and one-half parts of soda crystals in seventy-five parts of water. Use hot as a dip.

Fizeau[151] recommended making a 1 : 160 solution of gold chloride and adding gradually a solution of a carbonated alkali until the liquid becomes cloudy, when it is ready for use.

Elkington[152] found that if a platinum solution was made up by the methods given for his gold bath above, and a little of his gold solution added, objects hung in it were plated with platinum. Similar and betters results were obtained by using his regular gold bath and adding a little platinum chloride just before use.

A carbonate bath of totally different composition is recommended by Spon.[153] He dissolves ⅓ oz. of potassium bicarbonate and 4¼ oz. of gold (as chloride) in 3½ gal. of water, and boils for two hours. He also recommends a dipping bath containing 7 oz. potassium bicarbonate, 63 oz. potassium hydroxide, 3 oz. potassium cyanide and ⅓ oz. gold in 2 gal. of water. This

[148] Echo du monde savant, 1841, No. 666; Dingler Poly. J., 82, 122 (1841).

[149] Watt and Philipp, p. 167.

[150] Henley, p. 577.

[151] Sci. Am. Cyc., p. 188; Watt and Philipp, p. 177.

[152] Eng. Pat., Feb. 17, 1837; Repertory of Patent-Inventions, Dec., 1837, 354; Dingler Poly. J., 67, 270 (1838).

[153] I, 282.

is to be used hot, but gives a very thin coat. The same bath is given by Watt and Philipp.[154]

Von Ruolz, in the patent already mentioned,[155] included the solution of the double carbonate of sodium and gold in sodium carbonate, and also a solution of gold sulphide dissolved in potassium sulphide; and Dumas states that the latter gives the best results of any of von Ruolz's solutions. For electroanalysis a solution of 0.13 gm. gold in 15 c.c. of sodium sulphide (sp. g. 1.19) with a current density of 0.1 to 0.2 amp. per 100 sq. cm. at 60° C. is said to give a bright deposit, while a phosphate solution containing free phosphoric acid gave a brown deposit.[156] Withrow,[157] with the rotating anode, got good deposits from a solution of gold chloride in sodium sulphide under the same conditions as he used for the cyanide, and the method is recommended by Smith.[158] Perkin and Prebble[159] state that the sulphide method recommended by Smith gave them good deposits. It does not appear that this solution has ever been worked as a plating bath; its instability and the damage done by the hydrogen sulphide to other work in the shop would probably make it unsuitable.

Landois[160] recommends the use of a solution of gold cyanide in common salt.

Marino[161] prepares a bath for plating gold or silver on iron or steel by dissolving salts of the metals in solutions of sodium or potassium glyceroborobenzoate.

Brannt[162] recommends the use of an amalgam of mercury four parts, zinc two parts and gold one part mixed with eight parts of hydrochloric acid and one part of cream of tartar. Boil the object in the above bath(?) until it is of a bright gold color.

Linsenmayer[163] patents a solution from which he claims to precipitate an alloy of gold and aluminum. The bath is made in three parts: (A) 7 oz. of sodium phosphate, 1½ oz. salammoniac and 1 oz. of magnesia are dissolved in 10 liters of water.

[154] p. 168.
[155] Dumas, Compt. rend., 1841, No. 22 (Nov.); Dingler Poly. J., **83**, 125 (1842).
[156] Miller, J. Am. Chem. Soc., **26**, 1255.
[157] J. Am. Chem. Soc., **28**, 1350.
[158] p. 165.
[159] J. Chem. Soc., **86**, 370.
[160] Dingler Poly. J., **142**, 157 (1856).
[161] Eng. Pat., 22141; J. Soc. Chem. Ind., **31**, 394.
[162] p. 111.
[163] U. S. Pat., 231064, Aug. 10, 1880.

(B) 2 oz. sodium bicarbonate, ½ oz. common salt, ½ oz. of sulphur and 1 dwt. of acetic acid are dissolved in 5 liters of water. (C) 10 oz. potassium cyanide and 15 dwt. of alcohol are dissolved in 8 liters of water. The three solutions are mixed, boiled half an hour, cooled, and a solution of 2 oz. burnt alum in 1 liter of water is added, followed by an ounce each of aluminum and gold (as chlorides), 4 oz. potassium cyanide and an ounce of ammonia. The whole is boiled a half hour and filtered. It is to be electrolyzed at 180° to 200° F.

Baths to Produce Special Colors.

The problem of producing gold of abnormal colors is often met with, and the means adopted for its solution are of interest in connection with the projected discussion of the influence of the composition of the bath on the deposit. It is stated[164] that a plain gold bath can be made to give deposits of any color, from the pale 16-karat to 24-karat gold, and even coppery reds, by varying the temperature and the current density. The colors may be varied locally by placing the object about 1¼ in. below the surface of the bath and bringing the anode to the surface of the bath and immersing it more or less deeply over different parts of the object. Too much potassium cyanide gives ugly, pale deposits; too little gives red-brown ones. Hot baths are said to contain from 11 to 20 grains of gold to the quart, and considerable excess cyanide; such baths give a pale color at 90° F., a fine yellow at 120° to 130° F., and a reddish color at 140°. The smaller the current the paler the deposit; large current density makes the deposit red.

On the contrary, it is stated[165] that, while too high a current density will cause a dark, hard deposit, too much free cyanide may cause the same appearance, and a large excess will cause the production of a "foxy" red tint. Solutions too rich in gold deposit the metal too fast and in a non-adherent condition, and this is said to be intensified if an excess of free cyanide be present. Watt and Philipp[166] make similar statements, and add that the color of the deposit is affected by the motion of the articles in the bath. If the color is too dark, brisk motion of the articles

[164] Van Horne, p. 141.
[165] Bonney, p. 156; Hasluck, p. 115.
[166] p. 189.

in the bath will remedy it. They also state that the accumulation of organic matter in the bath affects the color, and that the presence of a small amount of such matter is often of advantage, especially in gilding the insides of vessels, where a rich, deep tone is required.

Green gold can be obtained[167] by the use of a platinum anode in the following solution: Water 10,000, sodium phosphate 200, sodium sulphate 35, potassium carbonate 10, and potassium cyanide 20 parts, in which is dissolved the chloride from 3.5 gm. gold. Boil down to half volume, filter, and dilute to original volume. To this add carefully some silver bath, and plate with 3 to 4 volts.

A bath for producing "sea-green gold" is made[168] by boiling together 6 gal. water, 20 oz. cyanide, 12 dwt. gold (in the form of fulminating gold), 3 dwt. silver (in the form of chloride), diluting to 10 gallons and making up to 10° Bé. by adding potassium cyanide. A saturated solution of sodium hydroxide and lead acetate is prepared, and four teaspoonfuls of it added to the above bath, which is then ready for use. Work at 160° F., with a low current density. The same author states that the addition of sodium arsenite to the bath for green gold gives work which is not permanent.

C. H. P.[169] recommends the following solution for green gold: Water 1 gal., cyanide 2 oz., gold chloride 9 dwt., silver chloride 3 dwt., used cold. The same author states[170] that green gold is usually made by adding a little sodium arsenite to the gold bath, and removing the black smut which forms on the object with bicarbonate of soda. He also states that some use lead carbonate for the green gold bath.

Hoffman[171] recommends the following bath for green gold: Water 1 qt., cyanide 3 oz., ferrocyanide 1 oz., potassium hydroxide 1 stick, salammoniac 1 oz., with 2 dwt. gold as chloride. Then add silver nitrate solution until the deposit shows green, and then sodium arsenite until a green smut is formed.

The mixing of gold and silver baths to produce green gold is

[167] Henley, p. 578.
[168] Schneider, Met. Ind., 9, 256.
[169] Met. Ind., 9, 479.
[170] Met. Ind., 8, 87; 9, 15.
[171] Met. Ind., 8, 464.

also recommended by Watt and Philipp,[172] Henley[173] and Keller.[174] The latter author recommends also the deposition of a coat of gold from a weak bath, and then the use of a silver anode until the desired tone is obtained.

Hoffman[175] also recommends for a light green gold: 1½ pints water, 3 oz. cyanide, 1 stick potassium hydroxide, 1 oz. salammoniac, 1 oz. ferrocyanide, 6 oz. of gold solution and 1½ oz. of 5 percent silver nitrate solution. Make the whole up to one quart, and use at 100° F. For a dark green gold he recommends the preparation of a solution of ½ oz. arsenious oxide and 6 oz. potassium cyanide in a pint of water, and its addition drop by drop to the above solution until the color is right. Five to ten drops are said to be enough to give an antique green gold. Wherever this author refers to "gold solution" he refers to a solution made from 10 dwt. gold (as chloride?) and ½ lb. potassium cyanide dissolved in water and made up to 30 oz., so that 3 oz. contain 1 dwt. gold.

For "rose gold" the same author recommends 1½ pints hot water, 3 oz. potassium cyanide, ½ oz. ferrocyanide, ½ stick potassium hydroxide, 15 grains salammoniac and 8 oz. gold solution, made up to a quart and used at 160° F. A little later[176] he recommends the following for cold rose solution: Warm water 3 pints, 10 oz. cyanide, 5 oz. ferrocyanide, 2⅓ oz. sodium carbonate, ½ oz. salammoniac and 9 oz. gold solution made up to a quart(!!) and worked at 60° F.

For the same purpose Stremel[177] recommends the solution, in a gallon of water, of 4½ oz. cyanide, 6½ dwt. of gold and 2 sticks of potassium hydroxide. This is to be used at 145° to 150° F. After rubbing the work in bicarbonate of soda, finish by flashing with cyanide 2 oz., gold 4½ dwt., water 1 gal. For cheap work he recommends a coat of copper, followed by a flashing in: Water 1 gal., cyanide 3½ oz., potassium hydroxide 1 stick, gold 4½ dwt. On spelter figures give a coat of copper and flash in: Water 1 gal., cyanide 2 oz., gold chloride 4½ dwt.

Red gold is obtained by adding a small quantity of copper to

[172] p. 205.
[173] p. 577.
[174] Elektrochem. Z., **16**, 243.
[175] Met. Ind., **8**, 292.
[176] Met. Ind., **8**, 345.
[177] Met. Ind., **8**, 463.

the gold bath.[178] A copper-gold anode may be used. For a cheap "14 K. solution" C. H. P. recommends[179] the solution of 3 oz. cyanide, 1 oz. gold chloride, ¼ oz. copper carbonate, ¼ oz. nickel carbonate and ½ oz. sodium bisulphite in a gallon of boiling water, boiling this for a time and replacing the water lost. Use an anode of fourteen parts gold, six parts copper and four parts nickel. Electrolyze hot, with 3 volts. If a lighter color is desired add more nickel.

Hoffman[180] recommends the following 14 K. solution: 1½ pints water, ¼ oz. copper carbonate, 3 oz. cyanide, 6 oz. of gold solution, 5 gm. sodium bisulphite, made up to a quart and used at 150° to 160° F. For a 14 K. solution to cover an 8 to 10 K. base, dissolve in 1½ pints of water 5 oz. of cyanide, 1 oz. copper carbonate, ½ oz. ferrocyanide, 1 oz. soda and 12 oz. gold solution, and work at 100° to 125° F.

For Roman gold the same author recommends the use of two solutions,[181] a finishing solution made by dissolving ½ oz. cyanide, 6 oz. of gold solution and 1 grain of salammoniac in 3 pints of water and diluting to make 1 quart(!), and a Roman solution made by dissolving 3 oz. cyanide, ½ stick of potassium hydroxide and 1 grain sodium acid sulphite in 3 pints hot water, adding 9 oz. of gold solution and water to make a quart(!). This is to be used at 160° F.; the objects are plated three or four minutes in the Roman solution, and then one-half minute in the finishing solution.

According to Stiehle[182] a good Roman gold bath is made by dissolving 2 oz. cyanide and 12 to 15 dwt. gold in a gallon of water. This should be used at 160° to 180° F. with 1½ to 2½ volts.

Kington[183] patented the deposition of a hard, durable alloy of gold out of a cyanide solution, using an anode containing 3 oz. gold, 40 oz. copper and 6 oz. German silver.

Watt and Philipp[184] state that Record's gilding bath, patented in 1884, consisted in the addition to the ordinary solution con-

[178] Watt and Philipp, p. 205; Henley, p. 577.
[179] Met. Ind., **10**, 384.
[180] Met. Ind., **8**, 345.
[181] Met. Ind., **8**, 114.
[182] Met. Ind., **8**, 462.
[183] Eng. Pat., 13750; J. Soc. Chem. Ind., **22**, 1299 (1903).
[184] p. 184.

taining 1 oz. gold of the following: 5 oz. nickel salts dissolved in about 2 gal. of water, to which about 12 oz. of cyanide are added and all ammonia boiled off.

For pink gold Spon[185] recommends gilding with a yellow color in a hot bath, passing through a mercuric solution, gilding to a red color in a hot mixture of ten parts of gold solution and three or four parts of copper solution, and then passing through a nearly exhausted pyrophosphate gold bath containing a little silver nitrate.

The following "sea-water gold solutions" are recommended by Hillman[186] for use where there is no wear on the object. Use a porous cup, with a piece of zinc in a 15° to 20° Bé. salt solution outside, connected to the work which hangs in the appropriate solution in the cup. The solutions are all based on three gallons of water. For polished yellow brass use 12 oz. ferrocyanide, 3 oz. potassium hydroxide, 3 oz. sodium carbonate and 12 dwt. gold. For dipped bright yellow brass use 12 oz. ferrocyanide, 6 oz. sodium phosphate, 1 oz. cyanide and 10 dwt. gold. For sand-blasted or matte yellow brass use 8 oz. ferrocyanide, 4 oz. sodium carbonate, 4 oz. sodium phosphate and 12 dwt. gold. For polished copper use 12 oz. ferrocyanide, 3 oz. sodium bisulphite, 6 oz. sodium phosphate and 18 dwt. gold. For satin-finished copper or copper-plated work use 12 oz. ferrocyanide, 6 oz. sodium bisulphite, 6 oz. sodium phosphate and 18 dwt. gold. For 10 to 18 K. gold or rolled plate use 6 oz. ferrocyanide, 2 oz. potassium carbonate, 4 oz. cyanide and 12 dwt. gold. For silver articles use 12 oz. ferrocyanide, 6 oz. sodium carbonate, 1 oz. potassium hydroxide and 12 dwt. gold. In each case the gold is to be converted to the neutral chloride or to fulminating gold, and added last. Heat the solution, allow to stand over night, and filter.

General Information.

Philipp[187] notes that if gold chloride be used in the preparation of the cyanide bath, and more added later to strengthen the bath, the character of the deposited gold steadily deteriorates, while if pure metallic gold be used instead of the chloride this

[185] I, 285.

[186] Met. Ind., 8, 28.

[187] Berliner Gewerbe-, Industrie- und Handelsblatt, **15**, 4; Dingler Poly. J., **96**, 334 (1845).

is not the case. The use of the double chloride of gold and sodium makes matters worse. The sodium chloride is evidently the cause of this effect.

Hasluck[188] states that the formation of a green slime on a gold anode is caused by the presence of an insufficient amount of free cyanide in proportion to the other ingredients and the current. As the solution ages the deposit becomes darker, either on account of the accumulation of copper in the solution or of impurities in the cyanide and the production of free potassium hydroxide in the solution.

Langbein[189] states that large amounts of organic substances such as can get into the bath from dust and other sources cause the bath to turn brown and the gold to deposit with a dark tone. The presence of lime compounds, from the use of impure water or from material used in cleaning the wares, causes ugly, spotted deposits.

Nicolaus[190] states that spotted or streaked deposits are due to an exhausted bath or poor circulation. If the bath is stirred, and the anode is not allowed to remain in the same position throughout the whole period, they may be avoided. Baths containing nickel, copper or acid are most likely to give trouble. Spots may also occur on account of improper cleaning.

The same author says that warm baths give a warmer tone and a matte surface. The bath should not be more than 75° C., and a lower current density is used than in the cold bath. Langbein[191] says that warm baths can be worked with a content of ¾ to 1 gm. gold per liter, but cold baths should contain at least 3.5 gm. per liter. Henley,[192] discussing the plating of German silver, says that if the solution intended for a hot bath is to be worked at a low temperature it should be diluted and a small anode used. The solution should be so weak that German silver does not reduce it *per se,* otherwise deposition is so rapid that the gold will peel while being burnished.

Van Horne[193] says that gold solutions may vary in strength from 15 to 320 grains per quart. Weaker baths require a larger

[188] p. 112.
[189] p. 383.
[190] Elektrochem. Z., **16**, 337; **18**, 145; Chem. Abs., **4**, 1429.
[191] p. 377.
[192] p. 578.
[193] p. 141.

proportion of free cyanide. A bath containing 10 percent of free cyanide will plate at three volts; without free cyanide 8 volts are required. Hot baths contain from 11 to 20 grains of gold per quart and a considerable excess of cyanide. Cold baths contain from 60 to 320 grains of gold per quart. Hot baths must be continually strengthened by adding a strong solution of one part chloride of gold and one to one and one-half parts of cyanide, as hot cyanide does not attack the gold anode. (?)

Coehn and Jacobsen[194] have investigated the electrode potentials in the electrolysis of gold solutions. They also state that a gold anode does not become passive in a pure concentrated solution of potassium cyanide, but does in the presence of sodium cyanide because of the formation of insoluble $NaAu(CN)_2$.

Hillman[195] says that there must be enough cyanide present in the bath to dissolve the gold anode and any slight film of oxide on the article. This can come from potassium cyanide, sodium cyanide or potassium ferrocyanide. Potassium ferricyanide is too unstable to be used. Too much cyanide causes the bath to attack the articles and take up base metal. Potassium hydroxide and sodium carbonate tend to give a deep yellow deposit, and should be used on light colored bases, such as silver or high brass. Sodium phosphate causes the deposit to lose some of its rich yellow, and should only be used on work that is apt to be water-stained or tarnished. It also tends to increase the uniformity of the deposit. Sodium bisulphite should only be used in plating copper, and in small quantities, as it gives a light canary yellow which looks like brass, but when a small quantity is used in plating on copper the light colored gold blends with the deeper colored copper to produce a good shade.

[194] Z. anorg. Chem., **55**, 321.
[195] Met. Ind., **8**, 29.

Part II. Electrodeposition of Silver.

Simple Salts.

Of the simple salts of silver the one most commonly used for general purposes is the nitrate. Much work has been done upon the electrolysis of this salt, especially in connection with the determination of the electrochemical equivalent of silver. It appears that the simple nitrate in neutral or acid solution does not give a deposit which is of a character suitable for electroplating. Luckow[196] seems to have been the first to study the electrolysis of this salt. He states that even from solutions containing 8 to 10 percent nitric acid the metal is precipitated in a very bulky state and a peroxide is formed on the anode. This peroxide has been studied by a number of authors.[197] This peroxide formation makes it impossible to secure satisfactory deposits for silver plating from a nitrate solution unless the anode and cathode liquids are separated by a diaphragm. By rapid rotation of the cathode under these conditions Snowdon[198] obtained fair deposits, and showed that the size of the crystal aggregates deposited decreased with increased current density. He also found that the addition of glue (0.5 to 10.0 gm. per liter of molar silver nitrate solution) gave smooth deposits which were always of a purple or yellowish-purple color. The deposit seemed to be a form of colloidal silver, and had no visible crystalline structure.

Bancroft[199] put forward the theory that the cause of loose deposits in the case of silver as well as other metals was the precipitation at the cathode of oxides, hydroxides and basic salts. That such precipitation would cause the formation of a bad deposit is not open to question, but that it is the sole cause of such formation may be doubted. Leduc and Labrouste[200] claimed to get a suboxide of silver at the cathode in the electrolysis of very weak solutions of silver nitrate, and Schuster and Crossley[201] claim that deposits of silver contain absorbed oxygen.

[196] Z. anal. Chem., 1880, 1.

[197] Sulc, Z. anorg. Chem., 12, 89; Leduc, Compt. rend., **135**, 23; Baborovsky and Kuzma, Z. Elektrochem., **14**, 196; Bose, Z. anorg. Chem., **44**, 237.

[198] Trans. Am. Electrochem. Soc., **7**, 143 (1905).

[199] Trans. Am. Electrochem. Soc., **6**, 27 (1904).

[200] Compt. rend., **145**, 55.

[201] Proc. Roy. Soc., **50**, 344; J. Chem. Soc., **64**, ii, 4.

Tanaeff[202] investigated the "activity" of the silver deposited by electrolysis of nitrate solutions, and stated that the most active deposit was formed from a solution containing 1.5 gm. silver nitrate and 5 c.c. nitric acid per 100 c.c. at 40° C. The "activity" was measured by the action of the metal on ferric sulphate. He states that the deposit was free from oxides, and amorphous, but that it is partly crystalline at higher temperatures, and almost wholly so if a 20 percent nitrate solution be used. Anode and cathode liquids were separated by a porous cup.

Sand[203] states that from a hot solution of silver nitrate he obtained a loose crystalline deposit, even with rotating electrodes. The deposit from the acetate was finer grained, and not dislodged by tapping. By addition of ammonia the deposits were made dense, and not loosened by tapping or scraping.

Hughes and Withrow[204] tried out several electrolytes for electroanalysis. With an acid solution of silver nitrate they obtained spongy deposits in all cases except when the voltage was kept below 1.4 and the amperage was extremely small. By the addition of ammonia and ammonium sulphate they obtained spongy deposits only when the amount of ammonia was small, but with a large amount of ammonia the deposits were good, and especially the first part of the deposit appeared to be bright as if burnished. Addition of ammonia and ammonium hydrogen phosphate gave crystalline deposits, as did also addition of nitric acid and ammonium acetate. The addition of sulphuric acid and glycerol gave coarsely crystalline and non-adherent deposits. The addition of 4 c.c. fluosilicic acid (sp. g. 1.06) per 100 c.c. gave a good deposit at 50° C. with a current of 0.1 amp. per 110 sq. cm., but when the current was doubled the deposit was spongy. All their work was done with stationary electrodes of platinum.

Fresenius and Bergmann[205] claim to get a compact deposit of silver for electroanalytical purposes from a solution containing 0.03 to 0.04 gm. silver as nitrate and 3 to 6 gm. free nitric acid in 200 c.c. They used a current of about 0.25 amp., and state that no peroxide was formed on the anode.

[202] J. Russ. Phys. Chem. Soc., **40**, 197; J. Chem. Soc., **94**, ii, 377.
[203] J. Chem. Soc., **91**, 386.
[204] J. Am. Chem. Soc., **32**, 1571.
[205] Z. anal. Chem., 1880, 324.

Jarvis and Kern[206] experimented with silver nitrate and fluosilicate solutions each containing 4 gm. silver per 100 c.c. They found that the fluosilicate gave better deposits than the nitrate. Gelatine (1 : 10,000 or 1 : 14,000) reduced the size of the crystals in the deposit, hence made the coat of silver denser and more coherent. With the fluosilicate, pyrogallol gave a black, non-adherent deposit, while tannin gave a dark but more adherent one. Resorcinol (1 : 1,700) improved the deposit slightly. None of these were of advantage with silver nitrate, and an excess of any of them is harmful. In silver methyl sulphate solution the addition of carbon disulphide, gelatine or gum arabic makes the crystals smaller and the deposit better. An electrolyte containing 4 percent silver as silver methyl sulphate, 4 percent methyl sulphuric acid, and gelatine or gum arabic in proportion of 1 : 12,000 or 15,000, has been patented by Betts[207] for silver refining. He states that in such a bath the current density should be about 10 amp. per sq. ft.[208]

The electrolytic refining of silver in a nitrate solution is practiced extensively.[209] The deposit is generally crystalline, and must be scraped off from the cathode. Foerster states that the electrolyte contains 0.5 to 1.0 percent silver and 0.1 and 1.0 percent free nitric acid, and the current density is 2.5 amp. per 100 sq. cm. at 1.5 volts. Kern states that the electrolyte contains from 2 to 4 percent silver nitrate, nitric acid as above, and that the current density is 20 to 25 amp. per sq. ft., although 40 to 50 amp. per sq. ft. has been used. It is stated that at the mint the anodic current density is only 7 amp. per sq. ft., and the cathodic current density practically the same. Silver cathodes are used, and by the addition of gelatine (1 : 8,000 to 10,000) the silver is made to deposit upon the cathode as a mass of solid coherent crystals, which do not grow over to the anode if the bath has the proper gelatine content. Gelatine must be added every day, but too much must be avoided, as it darkens the electrolyte and causes the deposit to be non-adherent. It is also stated that when wooden cells are used the action of the silver nitrate on the wood

[206] School of Mines, Quart., **30**, 100; C. A., **3**, 1495.

[207] U. S. Pat., 795,887, Aug. 1, 1905.

[208] See also Electrochem. Met. Ind., **3**, 145, and Trans. Am. Electrochem. Soc., **7**, 150 (1905).

[209] Kern, Met. Chem. Eng., **9**, 443; Foerster, p. 275.

causes the solution of organic material which makes the silver deposit in fine crystals.

Clark[210] has also patented a process of electrolytically refining silver, but the details of the process are not available to me.

A good deal of work has been done upon the silver coulometer, generally in a 10 percent silver nitrate solution. As the stress in such investigations is on the quantity of the deposit as related to the current, and the physical character of the deposit is not important so long as it is weighable, the work will not be reviewed here, but the reader who is interested is referred to the publications on this subject by the U. S. Bureau of Standards[211] and the work of other authors.[212]

Carhart has recommended the use of silver perchlorate in the coulometer.[213] Gore[214] says that the use of this electrolyte produces loose, bulky and silky crystals of silver and a black anode (peroxide?). The same author electrolyzed a solution of silver fluoride acidified with hydrofluoric acid, and obtained a crystalline deposit, while the anode became rough, gray and friable. With a solution of silver chlorate he obtained a deposit which was not very white, and a coating of peroxide was formed on the anode.

Mulder[215] passed a current through a saturated solution of silver selenate for 72 hours without any effect.

Marino[216] patents for silver and gold plating an electrolyte prepared by dissolving the salts of the metals in an aqueous solution of sodium or potassium glyceroborobenzoate, and states that it is particularly for use on iron and steel.

Mathers[217] states that silver may be deposited from a solution containing 5 to 10 percent silver perchlorate.

Parkes[218] melts silver chloride, hangs in it an anode and the

[210] Eng. Pat. 16,544, J. Soc. Chem. Ind., **4**, 751 (1884).

[211] Bull. Bureau of Standards, **1**, 21, 349.

[212] Gray, Phil. Mag., **22**, 389; Leduc, Compt. rend., **135**, 237; Kohlrausch, Pogg. Ann., **149**, 170; Bose and Conrat, Z. Elektrochem., **14**, 86; Kahle, Ann. Phys. Chem., **67**, 1, Abstr. in J. Chem. Soc., **76**, ii, 347; Richards, Collins and Heimrod, Z. Phys. Chem., **32**, 321; **41**, 302; Guthe, Electrochem. Ind., **2**, 406; Report of the Reichsanstalt, Z. Elektrochem., **17**, 34 (1911).

[213] Trans. Am. Electrochem. Soc., **9**, 375.

[214] Chem. News, **50**, 150.

[215] Rev. trav. chim., **22**, 387; J. Chem. Soc., **86**, 32.

[216] Eng. Pat., 22,141; J. Soc. Chem. Ind., **31**, 394.

[217] U. S. Pat., 931,944.

[218] Eng. Pat., Oct. 29, 1844, Repertory of Patent-Inventions, July, 1845, 32; Dingler Poly. J., **97**, 294 (1845).

object to be plated as cathode, and electrolyzes. Instead of silver chloride he states that a fused mixture of silver iodide (6 lb.) with potassium iodide (3 to 10 lb.) can be used. Lorenz[219] states that fused silver chloride, upon electrolysis, deposits silver as a brown mass. If zinc or lead chlorides are present the silver is still deposited before the other metal.

Arth and Nicolas[220] state that from a solution containing 1 percent free nitric acid as little as 0.0054 gm. silver may be deposited pure in the presence of 100 gm. lead, by electrolysis at 55° to 60° C., at not over 1.1 volts for 6 to 8 hours.

Smith and Moyer[221] have also separated lead and silver from a solution containing 15 c.c. nitric acid (sp. g. 1.3) in 200 c.c. According to Smith[222] silver can be separated from aluminum, barium, bismuth, cadmium, chromium, cobalt, iron, lead, magnesium, manganese, nickel, zinc, molybdenum, tungsten, osmium, selenium and the alkali metals in nitric acid solution by adhering to the proper conditions of temperature, acidity and voltage. In the separation of antimony from silver in the presence of nitric and tartaric acids the silver is deposited at a pressure of not exceeding 1.4 to 1.5 volts, but in a form not suited for weighing (*i. e.*, non-adherent?). The same thing appears to be true of ammoniacal solutions containing silver, antimony as pentoxide, and ammonium sulphate.

Classen[223] states that silver can be obtained as a white, strongly-adhering deposit on roughened dishes by electrolyzing a solution containing 1 to 2 c.c. con. nitric acid and 5 c.c. of alcohol if the voltage is carefully regulated to be between 1.35 and 1.38. As much as 2 gm. of silver may be so deposited.

Cyanide Baths.

What has been said about the purity of the potassium cyanide used in the early days need not be repeated. It is of application here as under gold. The same holds true for the use of distilled water and the methods of preparation of the various compounds of silver. The cyanide baths will be divided into groups

[219] Z. anorg. Chem., **10**, 78.
[220] Bull. soc. chim., **29**, 633.
[221] Z. anorg. Chem., **4**, 267.
[222] pp. 237 to 246.
[223] p. 201.

according to the silver salt which is used with potassium cyanide, and considered in the following order: Cyanide solution of silver nitrate, chloride, cyanide, and miscellaneous salts, so-called "bright" cyanide baths, general information on cyanide baths, and baths containing potassium ferrocyanide instead of cyanide.

Silver Nitrate in Potassium Cyanide.

These will be taken up in order of the increasing ratio of cyanide to silver, followed by baths where other salts are added. The addition of chalk is not considered to come under the head of addition of a salt when it is insoluble.

In a proposed silver voltameter Nernst and Farup[224] use a solution of 10 gm. silver nitrate and 15 gm. potassium cyanide in 100 c.c. water, electrolyzing in an atmosphere of hydrogen, and claim to get accurate results.

As a silver plating powder for Britannia metal Henley[225] recommends the use of one part of silver nitrate, two parts of potassium cyanide and five parts of chalk, to be rubbed on the well-polished articles, apparently wet.

Spon[226] recommends a plating bath containing 5¼ oz. silver nitrate and 9 oz. potassium cyanide dissolved in 2⅕ gal. water. For a dip without the use of the current he recommends 5¼ oz. silver nitrate and 17½ oz. potassium cyanide in 2 gal. water, also a solution of one part of silver nitrate and three parts of cyanide in water (amount not stated). Henley[227] recommends dissolving ten parts of silver nitrate and thirty-five parts of potassium cyanide separately in five hundred parts of water apiece, mixing, and dipping at 176° to 190° F. Stein[228] recommends a paste of one part silver nitrate and three parts cyanide. He states that neither the use of silver chloride nor the addition of common salt is advantageous. For a plating bath Hossauer[229] recommends thirty parts of silver nitrate and seventy-five parts of cyanide boiled fifteen to twenty minutes in two thousand parts of water. Five thousand parts of water are then added, the whole heated

[224] Z. Elektrochem., 8, 569 (1902).

[225] p. 587.

[226] p. 285.

[227] p. 597.

[228] Polytechn. Centralblatt, 1847; Dingler Poly. J., **105**, 27 (1847).

[229] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, 1843; Dingler Poly. J., **90**, 437 (1843).

to boiling, and filtered. He appears to have been the first to recommend the use of a silver anode. A bath of about the same composition is recommended by C. H. P.[230] It contains 4 to 5 oz. cyanide and 1 to 1½ oz. silver nitrate to each gallon, and is to be used at 190° F. as a dip for safety-pins.

A dipping bath containing a larger proportion of cyanide[231] is made by dissolving one part silver nitrate and five parts cyanide in one hundred and fifty-three parts of water, boiling and filtering. It is to be used cold. For an electrolytic bath the same author recommends one part silver nitrate, three parts cyanide and sixty parts water, boiled and filtered.

Söhner[232] recommends a solution of 75 gm. silver (presumably nitrate) and 400 gm. 90 per cent cyanide dissolved in 50 liters of water and used at 40° C. This bath is to be used until a preliminary deposit is obtained, after which if it is desired to hasten the deposition the work may be transferred to a solution of 30 gm. silver and 100 gm. 90 percent cyanide in 50 liters of water. This solution is to be used at 70° C. Spon[233] recommends a paste for silvering consisting of 1¾ pints of water, 2 oz. silver nitrate and 10½ oz. cyanide mixed with a sufficient amount of Spanish white to form a paste.

For electroanalytical purposes Foerster[234] recommends the use of about 2 gm. cyanide for quantities of silver up to 0.25 gm. The voltage required is 2.3 to 2.4. Spon[235] recommends two silver dipping baths of about the same composition: (1.) Water 5⅕ gal., silver nitrate 3½ oz., cyanide 21 oz., used hot; (2) water 16 oz., silver nitrate ½ oz., cyanide ¼ lb. The latter is for use on brass. Smith[236] recommends about the same conditions as Foerster, and shows that by rotating the anode the current density may be very largely increased.

Two silver plating pastes which appear to contain calcium nitrate are given. One[237] recommends the solution of 14 gm. silver in 26 gm. nitric acid, addition of a solution of 120 gm.

[230] Met. Ind., 8, 265.

[231] Dingler Poly. J., 116, 246 (1850).

[232] D. R. P., 35,852, July 10, 1885; Dingler Poly. J., 264, 328 (1887).

[233] p. 331.

[234] p. 240.

[235] p. 331.

[236] p. 108.

[237] Bayerische Industrie- und Gewerbeblatt, 1873, 91; Dingler Poly. J., 208, 47 (1873).

cyanide in a liter of water and 28 gm. powdered chalk. It is to be rubbed on the article, with or without the addition of powdered chalk. In the other,[238] 3½ oz. silver are converted to nitrate, 32 oz. cyanide dissolved in 25 lb. water added, and then 6½ oz. powdered chalk. This is to be rubbed on the object, or diluted with two parts of water for a dip. The same recipe is also given elsewhere.[239]

Nauhardt[240] patents a bath for silver-plating aluminum, containing equal parts of silver nitrate, potassium cyanide and ammonium phosphate. It is to be used cold.

Two baths found contain added carbonate. Spon[241] recommends for articles composed partly of iron and partly of copper: 6 oz. potassium hydroxide, 2 oz. cyanide, 3½ oz. potassium bicarbonate and ⅔ oz. silver nitrate dissolved in 9 pints of water. This is to be used hot, as a dip. Delatot[242] recommends for silver-plating iron a bath containing 100 lb. water, 2 lb. bicarbonate of soda, 2 oz. of either silver nitrate or chloride, 6 oz. potassium cyanide and 10 drops of hydrocyanic acid.

Peyraud and Martin[243] patent a silver-plating paste made by dissolving 10 gm. silver nitrate in 50 c.c. water, and 25 gm. potassium cyanide in 50 c.c. water, mixing, stirring and filtering. A mixture of 10 gm. powdered argol, 1 gm. mercury and 100 gm. powdered chalk is made, and moistened with above solution as needed. The same formula is given elsewhere.[244] Henley[245] recommends a paste for brass articles, made by making the same silver nitrate and potassium cyanide solution as above, and using it to moisten 100 gm. whiting and 400 gm. argol. The same author[246] recommends another paste, made by dissolving twenty-five parts of silver nitrate and fifty parts of potassium cyanide in two hundred parts water, and using this to moisten a mixture of twenty parts cream of tartar, two hundred parts Paris white and two parts of mercury.

[238] Advielle, Eng. Pat., Nov. 7, 1855; Repertory of Patent-Inventions, Aug., 1856, 148; Dingler Poly. J., **141**, 313 (1856).

[239] Brannt, p. 112.

[240] D. R. P., 100,786, Z. Elektrochem., **5**, 424 (1899).

[241] p. 331.

[242] Eng. Pat., Oct. 14, 1873; Dingler Poly. J., **215**, 471 (1875).

[243] Fr. Pat., Feb. 17, 1854; Dingler Poly. J., **134**, 129 (1854).

[244] Henley, p. 568.

[245] p. 587.

[246] p. 588.

A silver dip recommended by Spon[247] should perhaps be included under the next head, but as silver nitrate is used, it will be listed here. It is made by dissolving 15 gm. silver nitrate in 250 c.c. water, adding 30 gm. cyanide, and pouring into a solution of 15 gm. common salt in 750 c.c. water, and is recommended for iron articles.

Silver Chloride and Potassium Cyanide.

Langbein[248] states that in making up a silver bath either silver chloride or cyanide may be used, but that in strengthening old baths the cyanide must be used in order to prevent the accumulation of too much potassium chloride, which increases the density of the bath and gives a deposit with a coarse structure. Silver chloride is preferable for the original preparation of the bath, as it gives a bath of lower resistance, and the anodes dissolve more easily in such a bath. It is stated that the presence of potassium chloride in the bath facilitates the formation of the double cyanide of silver and potassium at the anode.

Bonney[249] states that there is no advantage in using the oxide or carbonate, and that the chloride gives a very white deposit, which is, however, especially likely to strip during burnishing. It is stated elsewhere[250] that, while the chloride is easier to prepare, the platers who do the best work use the cyanide. Chloride deposits do not burnish as well, and are more likely to strip. It is also stated that the solvent action at the anode is less in a bath prepared with chloride, and that it is more difficult to keep the bath in proper condition.

Watt and Philipp[251] recommend a bath of one ounce of silver, converted to chloride, dissolved in a moderate excess of potassium cyanide, filtered and diluted to a gallon. This is said to be very suitable for delicate white deposits, but not for ordinary work, as the deposit is likely to strip in burnishing. It is stated that if the bath be diluted and used with a moderate current and a small anode the deposit will generally adhere well.

It is stated[252] that the National Cash Register Co. uses a bath

[247] p. 331.
[248] p. 339.
[249] p. 128.
[250] Metal Ind., April, 1904; Electrochem. Ind., **2**, 200.
[251] p. 234.
[252] Met. Chem. Eng., **7**, 274.

of silver chloride in potassium cyanide for silvering on top of a half-hour coat of nickel.

Jewreinoff[253] fused eight parts of the dried ferrocyanide with three parts of dry potassium carbonate, and used a solution of the resulting mass to dissolve silver chloride, a slight excess of the chloride being used, as it is stated that an excess of potassium cyanide is not desirable. Another solution of indefinite cyanide content[254] contains one ounce of silver, as chloride, dissolved in a strong solution of cyanide and diluted to a gallon. The same author recommends the same solution with an ounce of silver, either as cyanide or as oxide, as alternative baths.

Pfannhauser's bath[255] contains 10 gm. silver as chloride and 20 gm. 99 percent potassium cyanide per liter. Langbein[256] recommends the same bath in his book as a bath for ordinary plating, and states that with the electrodes 10 cm. apart the voltage required is 1.25, and the current density should be 0.3 amp. per 100 sq. cm. He states that silver nitrate may be used instead of the chloride for preparing the bath, but prefers the chloride. For producing a strong coat he recommends a bath containing 25 gm. silver in the form of chloride and 40 gm. potassium cyanide per liter. The voltage required is 0.75, and the current density is the same as above. After the salts have been dissolved the bath is to be boiled for an hour, replacing the water boiled off. He states that during the boiling a small amount of a black substance containing silver is precipitated.

C. H. P.[257] recommends a "rich silver solution" containing 4 oz. silver chloride and 12 oz. potassium cyanide per gal. Elsewhere[258] he recommends a similar but more dilute solution for a general jobbing shop, containing 15 oz. silver chloride and 2¼ lb. potassium cyanide in 6 gal. water. If the solution is erratic when new, a little solution of carbon disulphide is added. (See under Bright Plating Baths). Van Horne[259] recommends a similar solution containing 3 oz. silver chloride and 9 to 12 oz. potassium cyanide per gallon. A somewhat similar solution[260] is made by

[253] Bull. de St. Petersburg; Dingler Poly. J., **89**, 125 (1843).
[254] Sci. Am., **24**, 305.
[255] Langbein, Z. Elektrochem., **9**, 979 (1903).
[256] p. 342.
[257] Met. Ind., **9**, 172.
[258] Met. Ind., **9**, 89.
[259] p. 127.
[260] Sci. Am. [I], **7**, 176.

dissolving a silver 25-cent piece, precipitating as chloride, and dissolving in a solution of 1 oz. potassium cyanide in a quart of water.

Fehling[261] recommends a solution of one part of silver chloride and six parts of potassium cyanide. Later[262] he recommends the addition of 84 gm. common salt to each pound of the above solution.

On some kinds of work, especially steel, it is customary to "strike" or give a preliminary treatment in a weak solution, generally poor in silver, and then transfer to another bath for the main operation. A formula for such a strike bath[263] contains ¼ oz. of silver chloride or cyanide dissolved in 1 lb. cyanide and a gallon of water. As a plating bath to follow this the same author recommends a solution of 1 oz. silver cyanide or chloride in 12 oz. potassium cyanide and 1 gal. water. C. H. P.[264] recommends as a strike solution ½ oz. silver chloride and 8 oz. potassium cyanide in a gallon of water. He states that electrolysis should take place in it at 1 to 1½ volts for only fifteen to thirty seconds before transfer to the regular bath. The latter contains little free cyanide, and is operated at a current density of 4 amp. per sq. ft. with less than 1½ volts. The same author states that the strike bath may vary in composition from 6 to 8 oz. cyanide and ⅛ to ¼ oz. silver chloride. Two 3″ x 8″ copper anodes and two silver anodes of half this area are used in the strike bath. In another place[265] the same author recommends striking in a solution of 8 oz. potassium cyanide per liter, using silver and copper anodes, but adding no metallic salts to the bath. No deposit should be formed on the article in this bath. This is to be followed by a second strike in a bath containing ½ oz. silver chloride and 4 to 6 oz. potassium cyanide per gallon, and the object then plated in a solution containing 4 to 7 oz. silver chloride and 7 to 10 oz. potassium cyanide per gallon. It is stated that a high current density is to be employed in these strike baths so there will be a vigorous evolution of hydrogen.

Reama[266] on casket hardware gives a light coat of nickel first,

[261] Dingler Poly. J., **86**, 350 (1842).
[262] Dingler Poly. J., **87**, 290 (1843).
[263] Sci. Am., **41**, 27.
[264] Met. Ind., **8**, 175; **10**, 494.
[265] Met. Ind., **9**, 313.
[266] Met. Ind., **10**, 371.

strikes in a solution of 8 to 10 oz. potassium cyanide and ½ oz. silver chloride per gallon, and plates in a "bright bath," *q. v.* For steel work the same author recommends striking in a solution containing 10 grains copper carbonate and 5 grains silver chloride in a potassium cyanide solution of 10° Bé. A 2″ x 8″ copper anode and a 1″ x 8″ silver anode are used. For strengthening this solution after use add only silver salts, not copper. This strike bath is to be followed by plating in a solution of 4 to 4½ oz. silver chloride and 15 to 18 oz. potassium cyanide per gallon. Another formula for a bath with a high proportion of cyanide[267] recommends the solution of the chloride from ½ oz. silver nitrate in ¼ lb. potassium cyanide and 1 gal. water.

For direct plating on cast iron Böttger[268] recommends a solution of 14 gm. silver nitrate, 225 c.c. water and 28 gm. potassium cyanide, diluted with 675 c.c. water containing 14 gm. common salt.

C. H. P.[269] recommends a bath containing 2½ oz. silver chloride and 6 oz. potassium cyanide per gallon, and says that ammonia should be added to this bath. The quantity to be added is not stated. If the deposit of silver is brownish, 1 oz. sodium thiosulphate is to be added to each 20 gal. of bath.

An alkaline strike bath[270] is recommended containing ¾ oz. silver chloride, 1 lb. potassium cyanide and 4 oz. sal soda in a gallon of water. This is to be followed by plating in another alkaline bath: 1 oz. silver as chloride, ¾ lb. potassium cyanide and 4 oz. sal soda in a gallon of water.

Schiele[271] patents a silver paste containing fifty parts silver chloride, one hundred and fifty parts potassium cyanide, fifteen parts aluminum nitrate, fifty parts thorium nitrate, one hundred parts cream tartar, three hundred parts water and three hundred and fifty parts chalk.

Fielder[272] patents a similar paste containing fifteen parts fused silver chloride, one hundred and fifty parts ammonia, thirty parts cream tartar, three hundred parts whiting, sixty parts potassium cyanide and five-tenths part zinc dust.

[267] Sci. Am., **40**, 410.
[268] Dingler Poly. J., **191**, 250 (1869).
[269] Met. Ind., **9**, 133.
[270] Sci. Am., **41**, 44.
[271] Fr. Pat., 320,154; J. Soc. Chem. Ind., **22**, 97.
[272] Eng. Pat., 6,589; J. Soc. Chem. Ind., **18**, 843 (1899).

Buchner,[273] for plating by dipping the object in contact with a piece of zinc, recommends a bath made by dissolving the chloride from ten parts of silver nitrate in seventy parts ammonia, forty parts soda crystals, forty parts potassium cyanide and fifteen parts common salt. This is then diluted to one thousand parts with water. This is almost the same as a bath for plating recommended elsewhere.[274] The chloride from 7 gm. silver is dissolved in 56 c.c. ammonia and mixed with a solution of 35 gm. crystal soda, 35 gm. potassium cyanide and 14 gm. common salt in 2 lb. water. This latter solution is to be warmed, the ammoniacal silver chloride solution added before it boils, the whole boiled about seven minutes, and filtered.

Silver Cyanide in Potassium Cyanide.

The earliest reference to the use of silver cyanide which I found was the recipe of Elsner,[275] who speaks of converting 14 gm. of silver to cyanide, dissolving this in potassium cyanide solution, and preferably adding sodium carbonate to make the solution alkaline.

Namias[276] recommends making up the bath according to the formula of the double cyanide, $AgCN.2KCN$, which would require one hundred and thirty-four parts of silver cyanide to one hundred and thirty parts of 100 percent potassium cyanide. As the bath becomes alkaline by use, he recommends the addition of a little potassium cyanide and monopotassium citrate from time to time. Langbein[277] recommends for heavy plating a solution of 25 gm. silver cyanide and 25 gm. potassium cyanide (98 to 99 percent) per liter, to be used with a current density of 0.3 amp. per 100 sq. cm. at 1 volt. The bath is to be boiled an hour after being mixed, replacing the water boiled off. Foerster[278] recommends the same solution, but gives the current density as 0.1 to 0.45 amp. per 100 sq. cm. He states that the decomposition of the bath during electrolysis produces principally potassium carbonate, together with oxalate, acetate and ammonia. Prac-

[273] Henley. p. 589.

[274] Kunst. u. Gewerbeblatt für Bayern, July, 1845; Dingler Poly. J., **97**, 383 (1845).

[275] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, 1842; Dingler Poly. J., **88**, 30 (1843).

[276] Monit. Scient., **18**, 487; J. Soc. Chem. Ind., **23**, 754 (1904).

[277] p. 340.

[278] p. 253.

tically the same bath is recommended by Pfannhauser,[279] who dissolves 25 gm. silver (as cyanide) and 27 gm. potassium cyanide per liter.

Elsner[280] recommends a 1 : 10 solution of the crystalline double cyanide of silver potassium, to which he adds one-eighth potassium cyanide, as the pure double salt will not plate with a silver anode on account of the formation of an insoluble film of silver cyanide upon it.

A somewhat similar formula is given by Langbein,[281] who also uses the crystalline double cyanide KCN.AgCN, dissolving 50 gm. of this and 10 gm. 98 percent potassium cyanide per liter. This bath is made by simply dissolving the constituents in cold water. The voltage and current density are as stated for his other bath above.

Several authors[282] recommend the solution of silver cyanide in one-fifth more cyanide than is requisite to just dissolve it and dilution to the desired strength (½ to 6 oz. per gallon). Bonney states that if articles are to be plated which are acted on readily by potassium cyanide a smaller amount of free cyanide must be used or else the articles must be "quicked" in a mercuric solution. There must be enough potassium cyanide to dissolve the anode freely and clean; excess will cause too rapid solution of the anode and the production of a loose deposit of silver.

Watt and Philipp[283] recommend the conversion of 1 oz. silver into cyanide and its solution in one-fourth more than the minimum amount of potassium cyanide solution, ½ lb. per quart. This is to be filtered and diluted to a gallon. Blount[284] states that the usual strength for a silver bath is 10 gm. silver cyanide and 15 gm. potassium cyanide per liter, but that the precise strength is not important. To prevent deposition of silver by action of the object on the bath a strike bath containing 3 oz. silver and 30 gm. potassium cyanide per liter is recommended. The object is to be treated in this for a minute with as high a current density as possible, and then transferred to the regular bath. A current

[279] Langbein, Z. Elektrochem. 9, 979 (1903).
[280] Dingler Poly. J., 112, 66 (1849).
[281] p. 342.
[282] Hasluck, p. 79; Weston, p. 118; Bonney, p. 121.
[283] p. 229.
[284] p. 260.

density of 4 amp. per sq. ft. is said to be suitable for the regular bath.

According to the Chemiker Kalender[285] a silver bath is made by dissolving 46 gm. potassium silver cyanide and 12 gm. potassium cyanide in a liter of water. The current density used should be 0.3 to 0.6 amp. per 100 sq. cm.

For ordinary plating, Langbein[286] recommends a solution of 200 gm. silver potassium cyanide and 100 to 120 gm. potassium cyanide (98 percent) in a liter of cold water.

The electrolytic preparation of the silver cyanide has also been recommended. Watt and Philipp[287] say that this gives one of the best baths for general purposes. They use 3 oz. potassium cyanide per gallon of water, and electrolyze with a copper cathode inside a porous cell, and a silver anode. An alternative procedure is the use of a large silver anode and a small silver cathode. They assume that the cyanide used is about 50 percent pure. They also suggest the neutralization of the potassium hydroxide formed at the cathode with hydrocyanic acid. Another bath[288] where the silver cyanide is made electrolytically, starts with a solution of 123 oz. potassium cyanide in 100 gallons of water, and dissolves a silver anode in this over night until the bath contains ½ oz. silver per gallon.

Another bath[289] is made by dissolving the cyanide from 5¼ oz. of silver nitrate in a solution of 8 oz. potassium cyanide in a gallon of water. It is stated that the specific gravity of this bath may vary from 5 to 15° Bé., and the bath still give good results.

Another recipe calls for 17½ oz. potassium cyanide, and 8¾ oz. silver, as cyanide, dissolved in 2⅕ gal. of water.[290]

Gresil[291] states that baths corresponding to the formula AgCN.2KCN are not always the best, and recommends for copper articles a bath containing 20 gm. silver cyanide and 30 gm. potassium cyanide per liter, and for tin or tinned articles a bath containing 50 gm. silver cyanide and 150 gm. potassium cyanide per liter.

[285] 1913 ed., **2**, 661.
[286] p. 342.
[287] p. 234.
[288] Sci. Am., **33**, 220.
[289] Sci. Am. Supp., 1881, 4936; Sci. Am. Cyc., 193.
[290] Spon, **1**, 334.
[291] Monit. Scient., **18**, 675; J. Soc. Chem. Ind., **23**, 905.

Another author recommends an alkaline bath,[292] containing 5 oz. silver cyanide, 2½ lbs. potassium cyanide and 8 oz. sodium carbonate per gallon. Another bath recommended by the same author contains 1 oz. silver cyanide and 4½ oz. potassium cyanide per gallon.

Hossauer[293] recommends the solution of the silver cyanide from 108 parts of silver in 1,540 parts of fused potassium ferrocyanide (crude cyanide) and 15,400 parts water. Practically the same formula appears elsewhere,[294] as a recipe requiring one part silver cyanide, ten parts potassium cyanide and 100 parts water.

"Trisalyt," a compound sold for use in making up baths for plating, appears to contain barium cyanide. According to the patent of the inventor,[295] the silver bath is made by dissolving silver oxide (one molecule), in a solution of barium cyanide (two molecules), to form a soluble salt of the formula $Ag_2(CN)_2.Ba(CN)_2.BaO$, or adding barium hydroxide to a solution of $BaAg_2(CN)_4$. This solution is treated with an acid so as to give a salt $Ag_2(CN)_2.Ba(CN)_2.BaCl_2$. Other alkalies, as potassium hydroxide, may also be used. The patent specifies the use of a mixture of an alkali cyanide, the cyanide of the metal, and a conducting salt.

Potassium Cyanide and Miscellaneous Salts.

Hardin[296] deposited silver with success from solutions made by adding silver acetate, silver benzoate or silver succinate to potassium cyanide.

Kemp[297] recommends a solution of one part of silver, as oxide, in a solution of eight parts of potassium cyanide and eighty parts of boiling water.

The Elkingtons[298] dissolve 5 oz. silver oxide and 3 lb. potassium or sodium cyanide in 30 lb. water, and use this cold, as an electroplating bath, or hot, as a dip. In the same patent they also mention the use of solutions of silver chloride, cyanide, or other

[292] Sci. Am., **42**, 59.
[293] Verh. d. Ver. Beförderung d. Gewerbefleisses in Preussen, 1843; Dingler Poly. J., **90**, 437 (1843).
[294] Sci. Am., **32**, 405.
[295] U. S. P., 693,378, issued to Emil Courant, Berlin.
[296] J. Am. Chem. Soc., **18**, 990.
[297] Chem. Gazette, March, 1847, No. 106; Dingler Poly. J., 1847, **104**, 315.
[298] Eng. Pat., G. R. Elkington and H. Elkington, Mar. 25, 1840; London J. Arts, Sept. 1841, 83; Dingler Poly J., **82**, 124 (1841).

insoluble salt in potassium cyanide, and solutions of silver iodide in potassium iodide, and of silver nitrate, oxide or chloride in ammonia, but they prefer the cyanide solution of the oxide in potassium cyanide. A fuller description of their patent elsewhere,[299] states that the quantity of water is 20 lb., instead of 30 lb., as given above.

Parkes[300] patented a solution in 1871, containing the oxide from 1 oz. of silver dissolved in a solution of 16 oz. potassium cyanide in 2 gal. of water.

Watt and Philipp[301], recommend conversion of the silver to carbonate, and solution of the precipitate in a moderate excess of a strong solution of potassium cyanide. The solution should contain about an ounce of silver per gallon. So long as the anode keeps perfectly clean while the work is being plated, the less free cyanide there is present, the better. A solution which has been in use for some time acquires a good deal of organic matter, becoming dark, and is then capable of bearing a larger proportion of cyanide without injuring the work than when it was fresh.

Watt and Philipp[302] also recommend as the very best solution for plating German silver a solution of the iodide formed from 1 oz. of silver in a moderate excess of potassium cyanide. They recommend making the iodide in a dark place or by lamplight. Whenever the anode becomes coated with a green film more cyanide must be added to the bath.

Baths for Bright Deposits.

The addition of a small amount of carbon disulphide to the silver bath seems to have a marked influence upon the character of the deposit. Watt and Philipp[303] state that this fact was discovered by Mr. W. Milward, of Birmingham, who kept the process a secret for a time, and then patented it jointly with a Mr. Lyons in March, 1847. There are two methods of adding the carbon disulphide: (1) 6 oz. of carbon disulphide are placed in a stoppered bottle, a gallon of plating solution added, and the

[299] Repertory of Patent-Inventions, Oct. 1841, 239; Dingler Poly. J., **82**, 375 (1841).
[300] Watt and Philipp, 232.
[301] p. 331. See also Sci. Am., **24**, 305.
[302] p. 232.
[303] p. 236.

whole shaken and allowed to stand twenty-four hours. Two ounces of the resulting solution are added to each 20 gal. of plating bath, the addition being repeated daily, on account of the loss by evaporation. This proportion gives a bright deposit; more gives a dead surface, very different from the ordinary dead lustre. (2) Take 1 qt. of ordinary plating solution, 1 pt. of strong potassium cyanide solution, 4 oz. carbon disulphide and 2 to 3 oz. ammonia, shake every two or three hours, then set aside for twenty-four hours. Add as under (1). Adding excess of the solution may ruin the bath. The same directions are given elsewhere.[304]

It is stated that the bath used in the plant of Elkington and Mason, in Birmingham, for bright plating was made as follows:[305] A bath containing 2 oz. silver cyanide and 1 lb. potassium cyanide per gallon was used, and about 1½ grains of carbon disulphide per gallon were added. The precipitation is slow, but the deposit is hard. The articles must not be moved in the bath, nor the latter stirred while in use, or else the coat will not have the desired polish. Spoons and similar ware are plated first in the usual bath, then finished with fifteen minutes plating in this bath. Instead of carbon disulphide a mixture of sulphur and collodion can be used, or a solution of iodine and guttapercha in chloroform, or some hydrocarbons, but it is stated that the disulphide is generally used.

C. H. P.[306] recommends a bath containing 3 oz. silver chloride and 6 oz. potassium cyanide per gallon, and the addition of a solution containing ½ oz. carbon disulphide, 8 oz. potassium cyanide and a pint of water to each 100 gal. of bath.

Blount[307] recommends the addition of 1 oz. of a saturated solution of carbon disulphide in the plating solution to each 10 gal. of the bath. He states that the current density should be higher than that normally used, agitation of the bath must be avoided, and the articles must be washed quickly after their removal from the bath. Another author[308] puts 1 oz. carbon disulphide

[304] Hasluck, 88; Bonney, 139.
[305] Mechanic's Mag., Nov. 1866, 269; Dingler Poly. J., **183**, 286 (1867).
[306] Met. Ind., **10**, 513.
[307] p. 260.
[308] Sci. Am. Cyc., 193.

in a pint bottle, fills this up with the plating solution, and adds a few drops of the mixture to the bath occasionally.

Smith,[309] to get a bright deposit, used a solution of potassium or sodium sulphocyanide, nearly saturated with silver sulphocyanide, to which he adds one of the following: Carbon selenide, iodine, nitrogen iodide, guncotton, the "sulphur salts" of arsenic, antimony or tin, "sulphur balsam," creosote, xanthates (especially potassium xanthate), compounds of carbon sulphide with methyl oxide, various acids, cyanogen, or sulphurous acid. In a note in Dingler, where this patent is abstracted, it is stated that the effect of carbon disulphide was noted by Elkington years before, so that there is no object in the use of any of the above substances.

Watt and Philipp[310] state that there have been several other substances proposed for bright baths, but no satisfactory substitute for carbon disulphide has been found. A solution of iodine and guttapercha in chloroform has been used, and is said to have a more permanent effect than carbon disulphide. The addition, every nine to ten days, of 1½ oz. each of potassium carbonate and bicarbonate to a bath containing 12 oz. cyanide and 3½ oz. silver per gallon is said to give a bright deposit. They also state that according to Planté bright deposits are obtained by adding a little silver sulphide to the bath. In the bath containing carbon disulphide they state that the articles first become bright on their lower surfaces, and the effect spreads upwards. As soon as they are bright all over they are removed and washed in boiling water, or else they will become dark. The bright deposit is put on as a superficial coat on top of the regular one, where the latter can not be conveniently burnished.

Langbein[311] refers to the addition of carbon disulphide and other similar substances to the bath, but states that he could not get any satisfactory results with them. He adds that the bath improves by absorption of small amounts of dust and organic matter from the air. He also recommends the addition of a few drops of salammoniac solution to the bath.

[309] Eng. Pat., June 7, 1849; Repertory of Patent-Inventions, Jan. 1850; Dingler Poly. J., **115**, 396 (1850).

[310] p. 237.

[311] p. 348.

General Information on Cyanide Baths.

In an article on the silver industry of Sheffield[312] it is stated that the process of silver-plating from a cyanide solution was discovered by John Wright in 1840. The Elkingtons heard of his process, and arranged with him for its use, patenting it in that same year and paying Wright a royalty of a shilling per ounce of silver deposited.

Philipp[313] ascribes the troubles met with in silver-plating to the impurities in the cyanide used, especially to iron, which was present on account of the fact that the cyanide used at that time was made by the fusion of the ferrocyanide.

Napier[314] investigated the decomposition of silver cyanide in the plating bath, and recommended the use of an excess of potassium cyanide to prevent the formation of silver cyanide as a solid on the anode.

Hasluck[315] states that too little potassium cyanide in the bath may cause the anodes to be covered with a black slime; too much is shown by a coarse crystalline condition of the anode, and the deposit is then apt to be loose on brass, copper and other metals which are easily soluble in an excess of potassium cyanide. He also states that an excess of potassium salts accumulating in the bath causes the deposit to be rough.

Watt and Philipp[316] state that a deficiency of potassium cyanide makes the bath grow weak on account of insufficient corrosion of the anode. Excess of potassium cyanide is necessary, but a large excess may cause the deposit to blister or strip.

Van Horne[317] states that too little potassium cyanide in the bath causes irregular results, while too much will give a yellowish plate, liable to blister and peel.

For maintaining the strength of the bath C. H. P.[318] recommends the addition of potassium cyanide to the extent of about 5 percent of the metal deposited. He says that the most uniform results are obtained by using as little excess cyanide as possible.

[312] J. Soc. Chem. Ind., **30**, 992.
[313] Dingler Poly. J., **92**, 239 (1844).
[314] Chem. Gazette, 1844, No. 44; Dingler Poly. J., **94**, 166 (1844).
[315] p. 82.
[316] p. 229.
[317] p. 127.
[318] Met. Ind., **10**, 37.

Langbein[319] states that insufficient excess of potassium cyanide increases the resistance of the bath. He gives the necessary excess of cyanide for a bath operated at normal current density as 10 to 12 gm. per liter. But if stronger current be used, this amount of cyanide may be too much and cause the deposit to be non-adherent. With very weak currents a larger excess of cyanide may be used without danger. For the direct plating of articles of tin or of alloys containing much nickel a greater excess of potassium cyanide must be used. For ordinary plating (thin coat), with a bath containing 10 gm. silver per liter, 5 gm. excess cyanide is enough, but 10 to 12 gm. does no harm and lowers the resistance of the bath. He states that after ten to fifteen minutes of plating with a moderate current density the ware should have a thin matte white coat; if this has not yet formed, or if it is a weak bluish-white, there is not enough potassium cyanide present. If this deposit, with proper current density, has formed in two to three minutes, and shows a crystalline structure or a dark hue tending to a gray-black, there is too much potassium cyanide present. If copper or brass articles become quickly and completely coated with metal on immersion, without electrolysis, there is too much potassium cyanide present. If the anodes remain pure white during the plating there is too much potassium cyanide present. If they become gray or blackish, and do not lose this color in fifteen minutes after shutting off the current from the bath, there is not enough cyanide present. Anodes should be grayish during electrolysis, and become white after completion of the process.

Jordis and Stramer[320] studied some baths working in regular shop practice, comparing them with similar idle baths. They conclude that the decomposition of baths made up with silver chloride is greater than that of those made up with silver cyanide. Among the decomposition products they recognized acetic and oxalic acids and carbonate. The carbonate increased more rapidly in used baths than in similar ones that were not used. Ammonia, ammonium cyanide and potassium formate are also present in old baths. They state that the influence of atmospheric conditions on the decomposition of the cyanide baths is large. The common

[319] p. 343.
[320] Z. Elektrochem., 9, 572 (1903).

statement that newly made baths give poor results was found to be untrue in their work.

With reference to the presence of potassium carbonate, Langbein[321] says that it is commonly present in the potassium cyanide as an impurity, and is also formed during the use of the bath. If more than 6 gm. per liter accumulates in the bath it must be removed by adding barium or calcium cyanide solution. He states that the effect of the presence of an excess of the carbonate is the same as that of an excess of potassium chloride.

It is stated[322] that sodium cyanide is now being used in place of potassium cyanide, and gives identically the same results. As would be expected, a somewhat smaller quantity of the sodium cyanide can be used on account of the lower atomic weight of sodium.

It is stated[323] that it is customary to mix some old cyanide bath with the new bath to improve its working qualities, and that some platers, instead of doing this, add ammonia.

Bonney[324] states that if the solution is contaminated with copper or other base metals, or deficient in silver, or if either current density or E. M. F. are too high, the deposit will be likely to be hard and dark. Too high a current may also cause a loose deposit. The addition of a brightening liquid may also cause the deposit to become hard and dark.

Pfannhauser[325] investigated the current efficiency of the precipitation of silver from the double cyanide plating solution, and found it to be practically 100 percent. Langbein[326] had previously found slightly lower results.

Wenzelmann[327] gives methods for analysis of plating solutions, and also recommends the removal of carbonate by the addition of barium cyanide.

The London Metallurgical Co. are said[328] to recommend the addition of cyanides of zinc and cadmium to the bath to increase the hardness and resistance of the deposit to atmospheric gases.

[321] p. 346.
[322] Brass World, 8, 192.
[323] Sci. Am. Cyc., 194.
[324] p. 132.
[325] Z. Elektrochem. **10**, 68 (1904).
[326] Z. Elektrochem., **9**, 979.
[327] Brass World, **6**, 87; C. A., **4**, 2618.
[328] Langbein, p. 349.

According to their patent the addition of 25 to 30 percent of zinc or cadmium to the silver completely prevents the tarnishing of the deposit and makes it hard and shiny. They use anodes of alloys of zinc and cadmium. Langbein states that several persons claim to have obtained good results with this method, but that he himself was unable to do so.

Netto[329] has patented a process of precipitating gold and silver from their cyanide solutions as obtained in metallurgical operations, consisting in acidifying these solutions, electrolyzing them and precipitating their content of noble metals, and then rendering them alkaline again for use in extracting a second portion of ore.

Ferrocyanide Baths.

Watt and Philipp[330] mention that solutions of silver cyanide in potassium ferrocyanide have been used, but give no formulas. Bonney[331] states that solutions containing potassium ferrocyanide do not dissolve the anode readily; this same complaint was made of such solutions in gold-plating.

Frankenstein gave a formula[332] for a silver bath containing ferrocyanide. He took one part silver chloride, five parts potassium ferrocyanide, five parts potassium carbonate, two parts of common salt and five parts of ammonia, dissolved in water (quantity not stated), boiled ½ to ¾ hour, and decanted from the residue.

Fehling[333] recommended a solution made by heating one part of silver chloride with eight to nine parts potassium ferrocyanide and 100 parts of water, on a water-bath for 3 to 4 hours.

Dumas[334] states that in the patent of von Ruolz the following formula was given for a silver bath: Silver cyanide 1 gm., potassium ferrocyanide 10 gm., water 100 gm.

Elsner[335] dissolved the chloride from 7 gm. silver by boiling in a solution of 84 gm. potassium ferrocyanide, 56 c.c. ammonia, and 2 lb. water, for at least an hour, replacing water lost by evaporation.

[329] D. R. P., Klasse 40, No. 88,957.
[330] p. 235.
[331] p. 128.
[332] Fehling, Dingler Poly. J., **87**, 290 (1843).
[333] Dingler Poly. J., **86**, 350 (1842).
[334] Compt. rend., Nov., 1841, No. 22; Dingler Poly. J., **83**, 125 (1842).
[335] Verh. d. Ver. z. Beförderung d. Gewerbefleisses in Preussen, 1842; Dingler Poly. J., **88**, 30 (1843).

Spon[336] recommended a bath to be used boiling hot as a dip, made from: Water 9 pts., potassium ferrocyanide 21 oz., potassium carbonate 14 oz., and silver (as chloride) 1 oz.

A solution ascribed to Watt[337] is made by dissolving 1 oz. silver (as cyanide), in a solution of 3 lbs. potassium ferrocyanide, and diluting to make a gallon.

Miscellaneous Chloride Mixtures.

Under this head will be grouped a number of recipes for pastes, etc., and some for plating baths, in which silver chloride, generally dissolved in an excess of common salt, plays the principal part.

Dernen[338] investigated the methods then in use, to find out what were the important constituents of silver-plating pastes and dips. He says that he found twenty-six recipes for the hot and cold processes. For the hot process, all recipes contain (1) either silver chloride or metallic silver which has been precipitated from solution by copper, (2) ammonium chloride, (3) common salt, (4) glass gall (sodium sulphate); and some also contained argol, mercuric chloride or zinc sulphate. For the cold process all recipes contained (1) either silver chloride, nitrate, or silver powder made as above, (2) common salt, (3) argol; and some contained alum, chalk, mercuric chloride, or free mercury. In the hot process the ware was thoroughly cleaned, painted with the paste, heated nearly to red heat over a charcoal fire, washed and scratch-brushed with argol. This process was repeated several times. The coat is said to have seldom been of a good white color, so objects were generally finished with the cold process. The boiling process, a modified form of the hot process, consisted in diluting the paste with water and boiling the articles in it. In the cold process, the articles were cleaned, warmed, the paste rubbed on, and the articles rinsed and scratch-brushed with argol. When used alone, this process gave a thin coat. Dernen experimented with the different materials recommended, and rightly concluded that the important thing in the process was to get some of the silver into a soluble form, from which it could be deposited on the brass. He found that the presence of ammo-

[336] Vol. **1**, 331.
[337] Sci. Am., **24**, 305.
[338] J. Prakt. Chem., **10**, 343 (1837); Dingler Poly. J., **65**, 196 (1837).

nium chloride was advantageous, as silver chloride was more soluble in it than in common salt. The presence of mercury (if volatilized later) made the coating penetrate the article and adhere well. He finally recommends for the warm process: 14 gm. silver chloride, 56 gm. common salt, 56 gm. ammonium chloride, and 56 gm. glass gall. For the cold process he recommends 14 gm. silver chloride, 84 gm. common salt, and 84 gm. argol, or preferably cream of tartar.

It is stated[339] that the preparations formerly made with silver chloride soon lost their efficacy on account of the action of light on the latter, and that common salt is a poor solvent for silver chloride, while ammonia attacks metals. Ferric and cupric chloride are said to have a protective action on the silver chloride and magnesium and aluminum chloride to have an accelerative action.

Becquerel[340] recommends the use of a saturated solution of silver chloride in a concentrated solution of common salt, and the electrolysis of this solution with a silver anode. This solution will give a thin coat by dipping, but a thicker coat is obtained with a battery. It is recommended a little earlier by von Kobell[341] as a dip for copper objects.

Landois[342] recommended the use of a saturated solution of silver cyanide in common salt, and the same solution was later recommended elsewhere.[343] A somewhat similar solution is also recommended,[344] where it is stated that brass may be plated by rubbing it with a mixture of silver cyanide, common salt, and cream of tartar.

Watt and Philipp[345] recommend the use of one and one-fourth parts common salt, one part silver chloride and three parts pearlash, made into a paste with a little water. The same formula with the addition of one part of paris white is recommended elsewhere.[346] Another similar formula[347] calls for the use of equal parts of silver chloride, chalk and pearlash.

[339] Z. angew. Chem., **14**, 672 (1902). See also Ger. Pat., 118,992.
[340] Compt. rend., April, 1844; Dingler Poly. J., **92**, 278 (1844).
[341] Dingler Poly. J., **85**, 342 (1842).
[342] Dingler Poly. J., **142**, 157 (1856).
[343] Sci. Am., (2), **15**, 385 (1866).
[344] Rev. chim. ind., **20**, 247; Spon, vol. **1**, 328.
[345] p. 238.
[346] Sci. Am., (2), **15**, 384; **11**, 163.
[347] Sci. Am., (2), **4**, 26.

A paste containing a very small excess of salt is recommended,[348] consisting of one part silver nitrate, one part common salt and seven parts cream of tartar. At the same time a formula[349] for using precipitated silver is given: Precipitated silver one part, common salt two parts and cream of tartar two parts. In each case water is to be added to make a paste.

Henley[350] gives a silvering paste for tin articles in two parts. The first part consists of three parts bismuth subnitrate and ten parts nitric acid, to which are added a solution of ten parts cream of tartar and ten parts hydrochloric acid in one thousand parts water. The object is immersed in this solution, and then removed, the pulverulent bismuth wiped off, and a paste of ten parts silver chloride, thirty parts common salt, twenty parts cream tartar and one hundred parts chalk is rubbed on. The latter part of this formula is almost the same as the formula of the same author for rubbing on brass:[351] This contains ten parts silver chloride, twenty parts common salt, twenty parts cream tartar, and water to make a paste.

A paste containing potassium binoxalate, presumably for dissolving the oxide from brass articles, is recommended by Spon.[352] It contains 3½ to 5 oz. water, 7 oz. silver chloride or the same amount of silver nitrate, 10½ oz. potassium binoxalate, 15 oz. common salt and 2¾ oz. salammoniac. A very similar formula is given elsewhere,[353] the only differences being in the omission of the alternative use of the silver nitrate, the specification of potassium oxalate instead of binoxalate, and the increase of the salammoniac to 3¼ oz.

Another paste with more salt is made[354] from three parts silver chloride, twenty parts cream tartar and fifteen parts of common salt.

Fiedler[355] patented a paste containing the silver chloride from 15 gm. silver nitrate mixed with 350 to 400 gm. tripoli or rouge, 80 to 100 c.c. acetic acid or vinegar, 300 to 350 c.c. sodium

[348] Sci. Am., (2), **11**, 163; Spon, 328.
[349] Apparently first given in Dingler Poly. J., **10**, 64 (1823).
[350] p. 588.
[351] p. 587.
[352] p. 328.
[353] Sci. Am., **43**, 18.
[354] Sci. Am., **44**, 273.
[355] Eng. Pat., 14,324 (1899).

chloride or potassium nitrate solution, and the whole diluted to a liter.

Hinque, Bonnin and Naviaux[356] patent a paste for rubbing on aluminum as a preparation to ordinary plating upon it, consisting of 10 gm. cream of tartar, 10 gm. silver nitrate and 150 gm. common salt.

For plating a large number of small articles cheaply it is recommended[357] to make a mixture of the chloride from 25 gm. silver, 1,250 gm. argol and 1,250 gm. common salt, place the articles to be plated in just enough water to cover them, and to each 5 liters of such water add 3 teaspoonfuls of the mixture. This gives a thin, adherent coat of silver, and can be followed by a coat applied with any regular bath.

Henley[358] recommends a paste containing sixty-five parts chalk, sixty parts sea salt, thirty-five parts cream of tartar and twenty parts silver nitrate. Grind all together in a mortar, not adding the chalk until the others are well powdered. Mix with water to make a paste.

Watt and Phillipp[359] take one part silver chloride, eighty parts cream tartar and, if desired, eighty parts common salt. Dissolve this in boiling water, and use hot as a dip. Glauber's salt, mercuric chloride and lime have been recommended as additions to this solution, but the authors express doubts of their value. They also recommend a paste of silver chloride mixed with at least an equal weight of cream of tartar and water to form a cream. A similar formula from Spon[360] calls for one part silver chloride, eighty-three parts common salt and eighty-three parts cream tartar.

Spon[361] also recommends dissolving together 2 oz. silver (as nitrate?), 3 grains of mercuric chloride, 4 lb. tartaric acid and 8 quarts of salt.

Barrat[362] patents several electrolytes, by the use of which he prepares plating baths electrolytically, dissolving the desired metal as anode. For silver he recommends a solution containing equal

[356] Fr. Pat., 348,399; Z. Elektrochem., **12**, 720 (1906).
[357] Erfindungen und Erfahrungen, **31**, 396; Z. Elektrochem., **10**, 906 (1904).
[358] p. 588.
[359] p. 238.
[360] p. 331.
[361] p. 328.
[362] Eng. Pat., June 15, 1843; London J. Arts, Feb., 1844, 28; Dingler Poly. J., **91**, 484 (1844).

parts of saltpeter, common salt and alum. Two other solutions, intended for use with either gold, platinum, lead, silver or palladium, are: (1) Four parts common salt, one part boracic acid, twenty parts water; (2) twenty parts common salt, seven parts tartaric acid, eighty to one hundred parts water.

Two pastes containing appreciable quantities of mercury salts are recommended,[363] the first one containing 2 oz. silver chloride, 1 oz. mercuric chloride, 3 lb. common salt and 3 lb. zinc sulphate. This mixture is made to a paste with water, and applied to the article, which must later be heated to drive off the mercury. The second formula contains 1 oz. silver as chloride, 6 oz. common salt, 6 oz. zinc sulphate and ¼ oz. mercuric chloride, and is used in the same way.

Göttig and Köttgen[364] patent a silvering mixture containing silver chloride, a solvent for silver chloride, and chlorides which are capable of readily giving off chlorine, such as ferric or cupric chloride. As an example they give: Silver chloride one part, potassium chloride three parts, cream of tartar two parts, ferric chloride two parts, and water three or four parts, to which tripoli, chalk, etc., may be added if desired. Another example is: Silver chloride one part, potassium chloride three parts, ferric chloride two parts, potassium stannic chloride one part, cadmium chloride two parts, clay eight parts, powdered chalk two parts, and water eleven parts.

Spon[365] also recommends a paste consisting simply of a mixture of silver chloride and whiting. (Proportions not stated.)

A bath for silvering small objects, such as metallic buttons, was recommended[366] at a very early date. It consisted of a solution of silver in nitric acid, to which is to be added a mixture of 1 oz. salammoniac, 1 lb. cream tartar, ½ lb. glass-gall (sodium sulphate), ½ lb. zinc sulphate and 2 lbs. common salt. This is to be used boiling hot as a dipping bath, evidently after adding a large amount of water.

Spon[367] gives two formulas for the use of precipitated silver. One contains 20 grains of this, with 2 dr. cream tartar, 2 dr.

[363] Sci. Am., (2), 4, 26.
[364] U. S. Pat., 663,340, Dec. 4, 1900.
[365] p. 328.
[366] Dingler Poly. J., 11, 504 (1823).
[367] p. 332.

common salt and ½ dr. alum. The other contains 40 grains precipitated silver, 3 dr. cream of tartar, 2 dr. salt and 40 grains alum. The latter formula is also given elsewhere.[368] He also recommended a paste of 30 grains silver nitrate, 30 grains common salt and 3½ dr. cream of tartar, moistened with water.

Miscellaneous Non-Cyanide Solutions.

Talbot[369] patented the electrolysis of a solution of silver chloride in sodium thiosulphate. Later Kendal[370] patented a mixture of a salt of silver, a thiosulphate and a silicious powder.

A non-poisonous paste[371] is made by dissolving one part of silver nitrate in eighteen to twenty parts of water, adding one-half part salammoniac and two parts of sodium thiosulphate. Finally add two parts of powdered chalk, and apply to the object with a brush. Henley[372] gives almost the same formula: Eleven parts of silver nitrate, dissolved in two hundred parts water, to which are added twelve parts salammoniac, twenty parts whiting and twenty parts sodium thiosulphate.

Bölsterli[373] patented a paste made by dissolving the chloride from 800 gm. silver nitrate in a solution of 3.3 kg. sodium thiosulphate in 30 liters of water, mixing this with 1.8 kg. 8 percent salammoniac solution and 8 kg. levigated chalk.

A silver dipping bath is made[374] by dissolving 1 oz. of silver nitrate in a quart of water and adding sodium thiosulphate until the precipitate first formed is dissolved, while by dissolving 1 oz. silver as chloride in an excess of sodium thiosulphate, and diluting to a gallon, a bath for electroplating may be made.

A silver dip recommended by Spon[375] contains fifty-five parts silver nitrate, ten parts sodium thiosulphate, sixty parts ammonia, one hundred parts chalk and one thousand parts water.

Poole[376] patented an electroplating bath containing 1 lb. silver as carbonate, dissolved in a solution of 8 lb. sodium thiosulphate

[368] Sci. Am., **4**, 26.

[369] Eng. Pat., Dec. 9, 1841; Repertory of Patent-Inventions, Jan., 1843, 47; Dingler Poly. J., **87**, 208 (1843).

[370] U. S. Pat., 724,108 (1903).

[371] Dingler Poly. J., **192**, 74 (1869).

[372] p. 568.

[373] Fr. Pat., 355,518; J. Soc. Chem. Ind., **24**, 1239 (1905).

[374] Sci. Am., **24**, 320, 305.

[375] p. 328.

[376] Eng. Pat., May 25, 1843; London J. Arts, Feb. 1844, 14; Dingler Poly J., **91**, 482 (1844).

in 2½ gal. water. This solution may be used as thus made up, or may be boiled for an hour first, thus precipitating some of the silver and decomposing some of the thiosulphate.

Thomas and Delisse[377] investigated the effect of ammonium salts in the silver bath, and found that no simple solution of a silver salt in an ammonium salt would give a satisfactory coat. They found that it was necessary to have a reducing acid present, such as sulphurous, phosphorous, hypophosphorous or thiosulphuric acids. The solution used must be acid for the best results. They recommend finally a mixture of ammonium acid sulphite and thiosulphate at 8° Bé., in which some silver salt is dissolved. The silver salts mentioned are oxide and chloride. Further directions for the preparation of this solution[378] include the formation of calcium polysulphide, its decomposition by a stream of sulphur dioxide until it is colorless and the solution is strongly acid, neutralizing this solution and precipitating the lime with ammonium carbonate, and finally making acid with sulphur dioxide again. No definite quantities are mentioned.

Watt and Philipp[379] ascribe to Roseleur the following process: Make a saturated solution of sodium acid sulphite, and add to it a solution of silver nitrate until the precipitated sulphite begins to be rather slow about dissolving. Use as a dipping bath for brass or copper articles, adding fresh silver nitrate from time to time to maintain the strength of the bath. This appears to be a slight modification of the formula given by Roseleur and Lanaux,[380] who recommend a solution of 1 kg. sodium acid sulphite in its own weight of water and the addition of 150 gm. of any silver salt to this.

Woolrich[381] saturates a solution of 28 lb. potassium carbonate in 44 lb. water with sulphur dioxide, precipitates 12 oz. silver nitrate with some of this solution, avoiding excess, and dissolves in one-sixth more than the minimum necessary amount of this sulphite solution.

Zinin[382] states that the double sulphites and thiosulphates have not been found satisfactory in practice, because they react with

[377] Compt. rend., April, 1852, No. 15; Dingler Poly. J., **124**, 287 (1852).
[378] Dingler Poly J., **125**, 157 (1852).
[379] p. 239; also Spon, 328.
[380] Technologiste, May 1847; Dingler Poly. J., **105**, 29 (1847).
[381] Mechanic's Mag., Feb., 1843, 146; Dingler Poly. J., **88**, 48 (1843).
[382] Dingler Poly. J., **259**, 26 (1886).

copper and precipitate silver upon the object in a non-adherent form and thus contaminate the bath with copper. Thiosulphates also soon begin to deposit silver sulphide spontaneously. He recommends a solution of 6.66 gm. silver nitrate in a liter of water, to which 500 gm. potassium iodide is to be added. A silver anode is to be used, and the current should be small enough so that iodine is not set free at the anode. He states that thick coats of silver can be deposited with this bath, and recommends it for making replicas in silver. The articles should be rinsed in 25 percent potassium iodide solution when removed from the bath. The same bath is given elsewhere[383] in English weights. Langbein[384] refers to this bath, and states that it gives poor results compared to the common cyanide baths.

Jordis[385] patents the use of lactates, or salts of any organic acid having the formula $C_n H_{2n} OH\ COOH$. The bath may be made by dissolving the lactate of the metal to be deposited, or by double decomposition of the nitrate of the metal and an alkali metal lactate, or by dissolving the metal as anode in a solution of lactic acid. He states that pure lactates give dark coatings, but by the addition of other alkali salts, or salts of calcium, magnesium or aluminum to increase the conductivity a lighter-colored deposit is secured. The bath gives especially good results with silver. He recommends the use of 1 to 3 percent silver nitrate, 3 to 5 percent ammonium lactate, and the addition of ammonia to an alkaline reaction. The current density per 100 sq. cm. should be 0.06 to 0.075 amp. Langbein[386] refers to this bath, and states that it gives good deposits, but that the only advantage it has over the ordinary cyanide baths is that it is non-poisonous.

Rockline[387] dissolves silver oxide in citric acid, and evaporates the solution to dryness. The dry salt is heated in a water bath, and dry hydrogen passed over it for a few minutes. It is then cooled and dissolved in cold distilled water. A muddy solution is thus obtained, which is used cold as an electrolyte. The hydrogen or the heated citric acid seems to have partially reduced the silver salt, as the author states that if this dark-colored solution

[383] Sci. Am., **58**, 292.

[384] p. 339.

[385] Eng. Pat., 11,298, J. Soc. Chem. Ind., 1896, 459; U. S. Pat., 570,544, Nov. 3, 1896.

[386] p. 339.

[387] Mechanic's Mag., Mar. 1843; Dingler Poly. J., **88**, 320 (1843).

is heated it clears and a dark sediment is deposited, and the solution is then not fit for use until retreated as above.

Spencer[388] dissolves silver bromide in a saturated solution of ammonium acetate, or can dissolve the silver in a mixture of bromine and alcohol, proceeding as specified under gold (*q. v.*). The ammonium acetate should be about thirty times the weight of the silver bromide. This solution is electrolyzed for plating purposes.

Gillette[389] worked out the separation of silver and copper electrolytically in an ammoniacal tartrate solution, using the rotating anode. As very rapid rotation of the anode was necessary to get an adherent deposit, the solution is evidently not adapted to plating work.

Gooch and Feiser[390] found that a solution of silver oxalate in ammonia would give a good deposit on a rotating cathode.

Several pastes have been invented in which magnesium or other electropositive metal is mixed with the other constituents. "Galvanit" is stated[391] to consist of a salt of the metal to be deposited, another salt capable of producing an aqueous electrolyte, and a metal electropositive to that to be deposited, as magnesium. "Voltite" is said[392] to be a powder invented by A. T. Firth, of similar composition to Galvanit. A patent[393] has been issued to A. Rosenberg for a similar substance, containing a salt of the metal, powdered magnesium, chalk and talc. Any reducible metal may be used. Skinner[394] patented a similar substance, composed of four parts silver nitrate, eight parts potassium cyanide, two parts sodium thiosulphate, one part zinc filings, twenty-four parts French whiting and forty-eight parts water.

Culley[395] patents a paste made by powdering an alloy of silver, nickel, tin and copper, and mixing this with a paste of ferrous carbonate, copper sulphate, nitric acid and water.

Böttger[396] recommends a dipping bath made by dissolving 3 dr.

[388] Eng. Pat., Mar. 8, 1841; Repertory of Patent-Inventions, Nov. 1841, 287; Dingler Poly. J., **83**, 378 (1842).

[389] J. Phys. Chem., **12**, 26.

[390] Am. J. Sci., **31**, 109.

[391] Met. Ind., **8**, 207.

[392] C. H. Proctor, Met. Ind., **10**, 77, 271.

[393] U. S. Pat., 970,755, Sept. 20, 1910.

[394] U. S. Pat., 511,810, Jan. 2, 1894.

[395] Eng. Pat. 17,081, J. Soc. Chem. Ind., **12**, 767.

[396] Frankfurter Gewerbefreund, 1840, No. 10; Dingler Poly. J., 1840, **78**, 60.

of silver nitrate in 2 oz. of aqua ammonia, but states that the time of first immersion must be very short, and the object must then be washed, rubbed, and the process repeated several times.

Tuck[397] dissolves one hundred and fifty-six parts of silver sulphate in a solution of seventy parts of ammonium bicarbonate, for German silver work. He uses one hundred and thirty-four parts of silver cyanide dissolved in the above amount of ammonium bicarbonate for plating articles of copper. Boil the silver salts in each case with the ammonium salt until solution ensues. For common German silver he recommends[398] a solution of ½ oz. silver sulphate in a solution of 107 grains of ammonium bicarbonate.

A very simple silver dip[399] is made by dissolving fifteen parts of silver nitrate and one hundred parts of crystallized sodium sulphate in water.

Another simple dip is made[400] by dissolving thirty parts of silver nitrate and thirty parts of potassium hydroxide in one hundred parts of water.

Brand[401] states that silver may be precipitated from a pyrophosphate solution acidified with nitric acid, but that this is in no way preferable to the cyanide solution.

Smith and Frankel[402] state that silver can be rapidly and satisfactorily precipitated from a solution of silver phosphate in ammonia, but not from a solution containing free phosphoric acid.

Bölsterli[403] patents a silver paste made by dissolving silver chloride in a reducing agent and adding powdered chalk.

Alloyed Deposits.

Field[404] investigated the problem of depositing silver and copper together from cyanide solutions, and showed that, although a very large proportion of copper was present, it did not begin to deposit until the silver content of the solution had fallen below 0.4 gm. per liter, and if the amount of silver fell below this the

[397] Eng. Pat., June 4, 1842; London J. Arts, July, 1843; Dingler Poly. J., **89**, 236 (1843).

[398] Watt and Philipp, 233.

[399] Sci. Am., **11**, 163.

[400] Henley, 588.

[401] Z. anal. Chem., **28**, 581.

[402] Am. Chem. J., **12**, 329.

[403] D. R. P., 173,912, June 11, 1906; Z. Elektrochem., **12**, 453 (1906).

[404] Trans. Faraday Soc., **6**, 1 (1910).

proportion of copper deposited increased very rapidly. The presence of free cyanide made it more difficult to deposit the two metals together. The deposits obtained were usually of a poor character, since the current density used was kept large in hope of increasing the amount of copper deposited with the silver.

For plating with an alloy of silver and nickel C. H. P. recommends[405] the use of the cyanides of nickel and silver dissolved in potassium cyanide. Such a solution has been patented by Marshall,[406] who recommends a solution of 1½ oz. double cyanide of nickel and potassium and 1½ oz. of the double cyanide of silver and potassium dissolved in a gallon of water. An anode of pure silver is used, and the bath is replenished in nickel salts from time to time by adding the double cyanide. Langbein[407] states that many authors recommend the addition of the double cyanide of nickel and potassium to the silver bath in order to deposit an alloy of silver and nickel. He himself tried out the process under varying conditions, but never got more than a trace of nickel deposited with the silver.

Campbell[408] has patented a process for depositing an alloy of silver and platinum. His first patent calls for the solution of thirty-six parts of platinum and sixty-four parts of silver in aqua regia and their precipitation by ammonium chloride as a gray powder. One ounce of this precipitate is dissolved in a gallon of water and enough cyanide to give a clear solution. In his second patent the proportions given are 30 and 70, and it is specified that the current should be of such a strength as to deposit 6 grains of metal per sq. ft. per minute. He claims that the plated surface will withstand the action of nitric acid and of sulphides.

General Information on Silver Plating.

Nussbaum[409] patents the prevention of the formation of crystalline electrolytic deposits of metals by adding a colloid, such as linseed oil, mucilage or salep, having the property of migrating to the cathode when the current is passed. He states that the colloid

[405] Met. Ind., 9, 395.
[406] U. S. Pat., 850,944; Brit. Pat., 8,560; C. A., 1, 1917, 2, 487.
[407] p. 349.
[408] U. S. Pat., 248,554, Oct. 18, 1881; 253,159, Jan. 31, 1882.
[409] U. S. Pat., 832,024.

acts as a screen wherever the current density tends to increase above that on the rest of the cathode.

Brown[410] states that the use of impure anodes lessens the rate of deposition of the silver, and may retard the solution of the anodes. He states that the government assay stamp of 0.999 fine does not guarantee freedom from trouble, as the remaining part in the thousand may be insoluble matter which will coat over the anode or make the solution dirty.

Kahlenberg[411] states that Faraday's law is valid for the electrolysis of silver solutions in pyridine, aniline, phenyl cyanide and quinoline, and that he obtained firm deposits from all but the last of these solvents. The current density used was 0.17 to 0.25 amp. per 100 sq. cm.

Langbein[412] recommends stirring the plating bath when heavy coats are to be given, especially when other salts have accumulated in it, in order to obtain a smooth deposit. By stirring the bath a greater current density can be used. The bath should always be well stirred at the close of the day's work.

Watt and Philipp[413] state that guttapercha should never be used for lining tanks which are to contain cyanide baths, as the cyanide has a solvent action on it, and it ultimately renders the solution a bad conductor. On acidifying such a bath the authors obtained brown clots of altered guttapercha.

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The material in the following list of books and journals has been completely covered in the foregoing article. Other journals were, of course, available, but have not been systematically searched, partly from lack of time and partly because they appeared unlikely to contain anything of value which would not be found in one of the abstract journals consulted[414] or copied in one or other of the technical journals.

[410] Met. Ind., **10**, 121.
[411] J. Phys. Chem., **4**, 349.
[412] p. 347.
[413] p. 287.
[414] Chemical Abstracts, Dingler Poly. J., J. Chem. Soc., J. Soc. Chem. Ind.

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University of Minnesota,
Minneapolis, Minn.

A paper presented in the Symposium on Electrodeposition of Metals, at the Twenty-Third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913, President W. Lash Miller in the Chair.

THE ELECTRODEPOSITION OF COBALT AND NICKEL

By Oliver P. Watts.

In accordance with a request from the President of the Society, this paper was undertaken with the intention of including all solutions used for the deposition of cobalt and nickel. Lack of time, however, has prevented such a thorough search of the periodical literature as could insure this result. Because of the difficulty of making intelligible yet brief abstracts of lengthy metallurgical processes in which electrolysis is often but a single step, the various processes and patents which deal with the extraction of these metals from their ores have been omitted.

ELECTRODEPOSITION OF COBALT.

Cobalt and nickel present such striking similarities in both physical and chemical properties that it is not surprising to find similarities in their behavior under electrolysis. In this connection Langbein[1] says: "For plating with cobalt, the baths given under 'Nickeling' may be used by substituting for the nickel salt a corresponding quantity of cobalt salt."

Hollard et Bertiaux[2] says: "In our numerous analyses we have never found any difference in electrolytic properties between nickel and cobalt." Many other writers give similar testimony.

While there is a general agreement in regard to the similarity of conditions and solutions suitable for the electrodeposition of cobalt and nickel, there is the widest disagreement concerning the relative hardness, color, etc., of these metals, as shown by the quotations which follow:

Brochet[3] says: "Cobalting has been proposed in place of nickeling when a deposit of the greatest hardness is desired."

McMillan[4] says: "The deposit of cobalt is similar to that of nickel; it is equally brilliant, but is somewhat harder."

1. For references, see the end of the paper.

On the other hand, Langbein says: "Cobalt precipitated from its chloride solution does not yield a hard coating."

Watt[6] says: "When deposited by electrolysis under favorable conditions, cobalt is somewhat whiter than nickel, but acquires a warmer tone after being exposed to the air for some time." . . . "Gaiffe says that, when deposited from a solution of the double sulphate of cobalt and ammonium it is 'superior to nickel in hardness, tenacity and beauty of color.' Wahl remarks: 'The electro-deposits of this metal which we have seen equal, if they do not surpass, those of nickel in whiteness and brilliancy of lustre.' Electrolytic cobalt[7] is somewhat softer than nickel."

S. P. Thompson[8] finds that articles plated with cobalt tarnish much less quickly in the atmosphere of London than silver or nickel plate; while Watt[9] quotes Stolba to the effect that cobalt salts treated like nickel "yield metallic deposits of a steel gray color, less lustrous than nickel and more liable to tarnish." In the same article Watt says: "I have invariably found that, while cobalt admits of being burnished without difficulty with a steel burnisher, nickel yields but little to the tool."

In the account of the deposition of nickel many authorities will be quoted in regard to the extreme difficulty or impossibility of obtaining deposits of that metal more than a few hundredths of a millimeter in thickness. E. Bouant[10] says: "Electrolytic deposits of cobalt are easily obtained, even of very great thickness, so that the electrodeposition of cobalt is as easy as that of copper."

A partial explanation of the above contradictions is given by Watt:[9] "The whiteness of electro-deposited cobalt depends greatly upon the nature of the electrolyte employed. Again, the density of current influences the color of the deposit; the strength of the solution also greatly affects the color of the deposit." It is evident that not only is the color of the deposit influenced by these and other factors, such as temperature, acidity, alkalinity, etc., but also that the hardness, brittleness and other physical properties of both cobalt and nickel are dependent upon the conditions above mentioned.

ELECTROPLATING WITH COBALT.

Concerning cobalt plating solutions, Watt says:[9] "Nearly all those who have devised formulæ for cobalt baths for electrodeposition prefer to employ solutions which are either neutral or more or less alkaline, but, so far as I am aware, in no case acid. . . . I have found that certain solutions were greatly improved when put in a faintly acid condition. . . . In working solutions which are more or less acid some little care is necessary to prevent the film from stripping or peeling off the receiving surface."

For ease of comparison the original composition of the baths which follow has been re-calculated to the basis of grams of solid taken per liter of water, where they were not already expressed in this way. Current densities are given in amperes per square decimeter, and temperatures on the centigrade scale.

1. Becquerel's solution:[11] 37.5 grams of cobalt chloride, neutralized by ammonia or potassium hydroxide, gives a brilliant, white, hard and brittle deposit. A very weak current must be used.

2. G. W. Beardslee's solution[12] consists of 30 to 45 grams of cobalt chloride per liter of water, made very faintly alkaline with ammonia. He claims that this bath gives a thick deposit which is very white, exceedingly hard, tenaciously adherent and not liable to tarnish. "I do not, however, limit myself to the precise method or agents above described, but employ any others which will produce similar results in substantially the same manner. What I claim and desire to secure by letters patent is: Electroplating with the metal cobalt so as to form a useful coating of this metal that is tenacious, compact, adherent, and flexible, and of sufficient thickness to protect the surface upon which it is deposited." Although plating with cobalt had been known for thirty years, the United States Government at this late date seems to have turned the practice over exclusively to Mr. Beardslee.

3. Boettger's solution[11] consists of 400 g. cobalt chloride, 200 g. ammonium chloride, 200 g. ammonia. It is claimed to give a brilliant deposit.

4. Watt[11] (page 519) recommends 37.5 grams of cobalt chlo-

ride, without any additions, as giving good deposits at low current density, but states that heavy deposits become dull.

5. Another solution by Watt[11] (page 519) consists of 37.5 grams cobalt chloride and 22.5 grams of ammonium chloride per liter. This gives a very white and very bright deposit, but requires a smaller current than No. 4.

6. The substitution of an equal weight of sodium chloride for the ammonium chloride causes the deposit to continue bright longer than in bath No. 5.

7. E. D. Nagel[13] patents the following for plating with cobalt, nickel, or both metals in combination:

"Four hundred parts by weight of pure sulphate of the protoxide of nickel (or cobalt) is combined with 200 parts by weight of pure ammonia to form a double salt, which I dissolve in 6,000 parts of distilled water, and add 120 parts ammoniacal solution of specific gravity 0.909. A platinum anode is used, and the solution is heated to 38° C."

8. Watt[11] (page 354) gives 30 to 45 g. of the double sulphate of cobalt and ammonium, made alkaline by ammonia, and states that the solution gives a fine white deposit.

Isaac Adams[14] says: "I have found that a solution made and used in the manner described in the books will not produce such a continuous and uniform deposit of cobalt as is necessary for the successful and practical electroplating of metals with cobalt. . . . I have found, further, that the simple salts of cobalt, such as are recommended by Becquerel and others, are not such salts as can be used in practical electroplating with cobalt. I have found out, also, that the simple salts of cobalt, when associated with another electrolyte—such as the chloride of ammonium, or the sulphate of ammonia, or the chloride of magnesium, or the sulphate of magnesia—can be used so as to produce good results in practical cobalt-plating.

"I have found, further, that, in order to produce the best results, the cobalt solutions should, in use, be neutral, and (except in covering poorly conducting surfaces) in no case acid. I find, further, that when solutions of cobalt are used—such as are mentioned in Smee—and contain an excess of ammonia, they become changed, by contact with the air, into such salts of cobalt as are not suitable for practical electroplating with cobalt. I

have found, further, that the electrodeposition of cobalt does not necessarily take place in solutions in which exist salts of alkalies—such as the nitrates of soda or potash, or free nitric acid."

Adams' solutions:[14]

9. 22.5 g cobalt chloride.
   15 g. ammonium chloride.

10. 22.5 g. cobalt chloride.
    15 g. magnesium chloride.

11. The sulphates of cobalt and ammonia.

12. The sulphates of cobalt and magnesia.

13. Watt[11] (page 354) gives 30 to 45 g. of cobalt ammonium sulphate, made alkaline by ammonia, and states that this gives a fine white deposit.

14. Watt[11] (page 518) also gives 37.5 cobalt sulphate per liter, and specifies a current density of 0.2 to 0.4 ampere per square decimeter.

15. Brochet[3] recommends 100 grams of the double sulphate of cobalt and ammonium, making 21 grams of cobalt per liter. Specific gravity 1.057. Specific resistance 22.1 ohms.

S. P. Thompson's[15] solutions:

16. 60 g. cobalt sulphate.
    30 g. magnesium sulphate.
    60 g. or less ammonium sulphate.

17. 100 g. double sulphate of cobalt and ammonium.
    50 g. magnesium sulphate.
    6.2 g. citric acid.
    12.5 g. ammonium carbonate.

These solutions are claimed to give "deposits of greater tenacity, density, and brilliance of tint, than have heretofore been obtainable with certainty." . . . "The solution for the deposition of cobalt may consist of the sulphate or chloride of cobalt, or of the double sulphate or chloride of cobalt and ammonium, to which has also been added the sulphate or chloride of magnesium, or other suitable soluble salt of magnesium, or a mixed soluble salt of magnesium and ammonium may be added to the solution of cobalt salts. Citrate of magnesium is a useful salt.

. . . Citrate of ammonium, or simply citric acid, may be added to the solution."

18. Maigne and Mathey[16] give:

28.6 g. cobalt chloride.
14.3 g. potassium cyanide.
143 g. sodium thiosulphate (hyposulphite).

The first two are dissolved separately, the solutions are mixed, the cobalt cyanide is washed, collected and dissolved in a solution of the thiosulphate in one liter of water.

19. The same authors (p. 334):

20 g. cobalt chloride.
10 g. potassium sulphocyanide.

20. Kayser's[17] solution:

67 grams cobalt sulphate.
67 grams ammonium sulphate.
33 grams boric acid per liter.

21. Langbein's[5] solutions consist of:

40 grams of the double sulphate of cobalt and ammonium.
20 grams boric acid.

At an E. M. F. of 2.5 to 2.75 volts, and a current density of 0.4 ampere per square decimeter, this bath is claimed to give a hard deposit suitable for electrotypes.

22. The solutions of Joseph Vandermersch[18] for the deposition of cobalt, nickel, copper, brass, manganese, cadmium, zinc and other metals are claimed to give deposits of any thickness and any weight. He says: "Heretofore in depositing nickel on iron and copper it has been possible to get only thin coatings (0.01 to 0.02 mm.). I obtain thick deposits by adding to a solution of nickel (or cobalt, etc.) sulphate as a base, one or several acids—benzoic, salicylic, boric, gallic, pyrogallic, and others of similar qualities—which gives a perfectly pure and white nickel deposit, but still in thin films only.

Therefore I add to the above bath 10 drops per liter, more or less, of sulphuric acid, and get deposits of any thickness and

of any weight. I may also add sulphurous, perchloric, chloric, formic, lactic, acetic, or other acid instead of sulphuric and get a similar effect. But sulphuric acid is best.

The same results are obtained with cobalt.

The process applies not only to nickel sulphate, but also to nickel chloride, nickel nitrate and all other nickel salts.

Instead of benzoic acid, etc., any compounds of these acids may be used, *e. g.,* calcium benzoate, etc. The chlorides, bromides, iodides, or other compounds of these acids may be used instead.

In the second operation, the sulphuric, sulphurous, or other acid may be replaced by compounds of salts of these acids, *e. g.,* sulphates. The sulphuric, lactic and other acids may be replaced by any other acid, provided they contain oxygen, and not only acids may be used for this purpose, but also all bodies capable of being added to the bath, provided they contain oxygen, such as alcohols, ethers, aldehydes, gums, sugars, creosote, glycose, glycerine, etc.

The second operation may take place before the first, the same result being obtained.

Acids capable of furnishing in a single operation the deposit of required thickness may, if desired, be employed, *e. g.,* phosphoric, permanganic, manganic, or other acids which are highly oxygenated, and which, when added to the nickel salts of any kind, give an unlimited deposit; but this result is far from equaling that of benzoic, aromatic and oxygenated compounds, superoxygenated by another body as above described. . . . It is however in all cases required as a total result that the bath be so constituted that it forms an ether, an alcohol, or an oxygenated acid, or an oxygenated compound in such a manner that hydrogen produced in consequence of decomposition of water by the electric current, is absorbed by the composition of the bath."

23. M. Kugel[19] deposits "tough, rollable, cobalt or nickel of any desired thickness by adding to any desired nickel-salt (or cobalt) solution, a strong mineral acid which is not changed in its chemical composition by the current. The most suitable acids are perchloric, perbromic and sulphuric. The acid concentration ranges from 2 to 20 percent normal or 1 to 10 grams per liter. The temperature must be kept above 30° C., and

current densities of 10 to 20 amperes per square decimeter may be used without harm to the deposit,—"a correspondingly lively movement of the electrolyte, in order to mix well, being of course necessary."

24. Alexander Classen[20] deposits more rapidly and compactly than has heretofore been possible, the metals cobalt, nickel, copper, iron, zinc, cadmium, bismuth, lead, tin, and antimony, by converting solutions of the chlorides or sulphates, by means of a solution of neutral potassium oxalate, into soluble potassium double salts. A suitable bath for cobalt consists of:

50 grams cobalt sulphate.
80 grams ammonium oxalate.
20 grams potassium oxalate.
1 liter water.

The baths are used hot.

25. E. Placet and J. Bonnet[21] claim the employment of polyatomic acid salts, alone or mixed with neutral salts, to obtain deposits of cobalt, nickel, chromium, aluminum, copper, iron, tungsten, molybdenum, antimony, tin, silver, etc., and the alloys of these metals electrolytically. They specify particularly the use of the bisulphates, biphosphates and biacetates" (?), and give the following bath for the deposition of chromium:

100 to 150 g. chrome alum.
100 to 150 g. acid sulphate of potassium, sodium, or ammonium, per liter of water.

It is evident at a glance that several of the metals listed cannot be deposited from these baths, and there is, from the chemical standpoint, no reason why the use of an acid salt should prove any more beneficial than equivalent amounts of the free acid and normal salt. The substitution of acid salts for free acid is claimed as the particular merit of the invention.

Watt[22] experimented with many different solutions for the deposition of cobalt. Those which he considered best were published in his book, and have already been mentioned in this paper. The others follow:

26. Cobalt acetate faintly acid gives a deposit which, at the end of an hour, is very bright, and pure white.

27. Cobalt and ammonium acetates gives a dull, brownish deposit.

28. The same as No. 27, made slightly alkaline, gives the same result as No. 27.

29. The same as No. 27, strongly acidified by acetic acid, gives a brilliant white deposit for two hours.

30. Cobalt citrate, acidified, gives a bright, but slightly yellowish deposit, and good anode corrosion.

31. Cobalt and ammonium citrates, neutral, gives a dull and dark deposit.

32. The same as No. 31, but acidified, gives a bright deposit. After 12 hours deposition the deposit is dark gray and nodular. The single citrate is better.

33. Cobalt borate, neutral, gives a bright and very white deposit, which finally loses its lustre and becomes dull. Gas is evolved at the cathode.

34. Cobalt tartrate, neutral, gives a deposit which turns black at the end of 10 minutes.

35. Cobalt tartrate, acidified, gives a bright and white deposit, and good anode corrosion.

36. Cobalt and potassium tartrates made by dissolving cobalt carbonate in a hot solution of cream of tartar, gives a white deposit, streaky on the front, but good on the back of the cathode. The result was the same in three different trials.

37. Cobalt phosphate gives only hydrogen at low current density. At higher currents a good deposit is obtained and much hydrogen is evolved.

38. Cobalt carbonate dissolved in a solution of ammonium carbonate gives at first a brilliant white deposit, becoming dull in 10 minutes. There is a vigorous evolution of hydrogen.

39. Cobalt salicylate gives a dark, but polished deposit.

40. Cobalt nitrate, a weak solution, gives on brass a malachite-green deposit of great beauty, which falls from the plate in transparent flakes.

41. Cobalt and ammonium nitrates gave a thick green deposit on brass.

42. Cobalt carbonate and sodium pyrophosphate were heated together, producing a solution of faint pink color. This gives a very adherent, dark deposit along with much hydrogen.

43. 42 g. cobalt sulphate and 30 g. potassium sulphate per liter, heated, gives a bright deposit, which peels off in 20 minutes Gas is evolved at both electrodes.

44. 42 g. cobalt sulphate and 18 g. magnesium sulphate per liter gives a bright and remarkably white deposit which becomes dull after a long time. No gas is evolved.

45. Excess of oxalic acid, added to a solution of cobalt sulphate, gives no deposit at low currents, but a bright deposit with evolution of hydrogen at high current.

46. Cobalt oxalate digested with a warm solution of ammonium carbonate gives no deposit of metal with one or two Daniell cells, but with three cells gives a brilliant, silver white deposit, and much hydrogen. In 15 minutes the deposit is streaked and in 30 minutes it is covered with dark streaks except on the edges.

47. Cobalt carbonate and potassium carbonate evolves much gas and yields a dark, smooth deposit of cobalt.

48. Cobalt sulphate and excess of ammonia gives a dark deposit. No gas is evolved.

49. Cobalt hydrate is very sparingly soluble in a strong solution of potassium cyanide, and three Daniell cells give only a trifling film of cobalt, and much gas.

50. Cobalt sulphocyanide. Potassium sulphocyanide, dissolved in alcohol, was added to a solution of cobalt sulphate, the clear solution decanted from the potassium sulphate, evaporated to dryness, and the residue dissolved in water. Three cells gave a slight deposit of cobalt on brass.

Many "per-salts" were tried. Calcium hypochlorite solution was added to a solution of cobalt sulphate, and the precipitate was washed and dissolved in the desired acid.

51. Cobalt per-citrate, tartrate, oxalate, acetate, chloride, sulphate, phosphate and borate all give bright, adherent deposits with three cells. Gas is evolved.

Gaiffe[5] has proposed the use of cobalt instead of nickel for facing valuable electrotypes on account of the complete solubility of the former metal in dilute sulphuric acid, thus permitting the removal of the film of cobalt and its replacement by a fresh deposit without injury to the copper.

DEPOSITION OF AN ALLOY OF COBALT AND NICKEL.

Owing to the difficulty of separating cobalt and nickel electrolytically as well as chemically, it should be an easy matter to deposit an alloy of the two metals. Nagel[23] deposits an alloy of the metals from a mixed solution of their ammonium double sulphates, made alkaline by ammonia, and heated to 40° C. He uses a platinum anode.

A similar trial was made in the experimental laboratory of the Brass World[24] for the purpose of getting a deposit harder than nickel, "since alloys are always harder than pure metals." The electrolyte consisted of a solution of 70 parts nickel sulphate, 30 parts cobalt sulphate, with ammonium sulphate sufficient to form double salts, acidified by boric acid and made up to 6° Bé. (sp. g. 1.0432). E. M. F., 2 volts. The deposit contained both nickel and cobalt, and was very hard. It was suggested for facing electrotypes, as the electrolytic iron commonly used, rusts.

The writer found in his filing cabinet another bath, from an unknown source, which is claimed to deposit the hardest alloy of the two metals, consisting of 75 percent nickel and 25 percent cobalt. The bath consists of:

Nickel ammonium sulphate	147	grams
Cobalt ammonium sulphate	40	"
Ammonium sulphate	56	"
Water	1,000	"

The following bath is given by Langbein[5] (p. 307):

Nickel ammonium sulphate	53	grams
Cobalt ammonium sulphate	13	"
Boric acid, cryst.	22	"
Water	1,000	"

The only obstacle to the general use of cobalt in place of nickel for plating appears to be its high price. Rumors have frequently reached us that cobalt was about to be put on the market at the same price as nickel. Fink[25], in 1912, says that cobalt can be bought for less than one-third what it cost ten years ago, yet in that same year the metal purchased for use in the writer's laboratory cost $5 per pound, just a dollar higher than it cost two years before, while in 1889 Watt, in England, bought the metal in the form of anodes for only $3.90 per pound.

In an account of the Cobalt mining district Gibson[26] says: "The enforced production of cobalt from these mines has brought about a reduction in the price of cobalt oxide and is likely to lead to still further reductions."

ELECTROCHEMICAL ANALYSIS.

Solutions for Estimation of Cobalt:

52. The double oxalate of ammonium and cobalt according to Classen:[27]

0.3 g. cobalt, present as sulphate.
4 to 5 g. ammonium oxalate.
120 c.c. in volume.
1 ampere per square decimeter.
2½ to 3½ hours at 60 to 70° C.
3.1 to 3.8 volts.

Perkin[28] (page 98) states that the deposit contains carbon.

53. Solution of Fresenius and Bergmann. Classen[27] gives:

0.5 g. cobalt as sulphate.
5 to 6 g. ammonium sulphate.
40 c.c. ammonia (s. g. 0.96).
150 to 170 c.c. in volume.
0.7 ampere at 20° to 25° C.

The presence of chlorides, nitrates, fixed organic acids and magnesium compounds acts injuriously. Neumann[29] (page 113) states that this is the only solution employed in practical analysis.

54. Cobalt and ammonium chlorides have been proposed by Oettel. According to Neumann[29] (page 112) a suitable solution is:

1 g. cobalt chloride (0.248 g. cobalt).
5 g. ammonium chloride.
30 c.c. ammonia.
150 c.c. total volume.
1.5 amperes.
5 to 6 hours.

For the determination of cobalt a larger amount of ammonium chloride is required than in the case of nickel. The presence of nitrates is harmful.

55. Cobalt potassium cyanide is stated by Smith[30] (p. 129) to give complete precipitation. He adds 0.1 g. more of potassium cyanide than is necessary for precipitation and re-solution.

2 g. ammonium carbonate.
150 c.c. in volume.
1.5 amperes at 60° C.
6 to 6.5 volts.
3½ hours.

Neumann[29] (p. 113) states that it is impossible to secure a quantitative separation of cobalt from solutions containing an excess of potassium cyanide.

56. Neumann[29] (p. 112) states that exact results are given by:

1 g. cobalt sulphate (0.21 g. cobalt).
15 g. ammonium carbonate.
2 to 4 c.c. ammonia.
150 c.c. total volume.
1 ampere at 3.7 to 3.9 volts.
2½ to 3½ hours at 50° to 60° C.

57. Perkin[28] (p. 97) adds 3 g. ammonium tartrate to the solution of the cobalt salt, begins electrolysis at 0.2 ampere, and after an hour increases the current to 1 ampere per square decimeter. Time, 4 to 5 hours. The deposit often has a brilliant, burnished appearance. The results are slightly high, owing to a small amount of carbon being deposited with the cobalt.

58. Perkin[28] (p. 98) claims that the most accurate results are obtained by adding to the solution of the cobalt salt:

2 c.c. of a 5 percent solution of phosphoric acid,
20 to 25 c.c. of a 10 percent solution of di-hydrogen,

sodium phosphate, stirring during the latter addition to prevent precipitation of a double phosphate. Hydrogen di-sodium phosphate cannot be used on account of the formation of an almost insoluble cobalt salt. Electrolysis should begin at 0.2 ampere in the cold solution. After an hour the current may be raised to 1 ampere and the solution warmed to 60° C. If a brown deposit forms on the anode it may be removed by adding 0.1 to

0.2 gram of hydroxylamine sulphate or chloride. Formaldehyde acts more slowly. Time, 4 to 6 hours. The deposit is usually brilliant.

59. Vortmann[30] adds tartaric or citric acid and an excess of sodium carbonate to the solution of the cobalt or nickel salt, then electrolyzes at 0.3 to 0.4 ampere. The deposit may contain traces of carbon.

60. Smith[30] (p. 129) obtains perfectly satisfactory results by adding an alkaline acetate to the cobalt solution. For rapid precipitation with a rotating anode he uses (p. 135):

Cobalt sulphate = 0.331 g. metal.
25 c.c. ammonia.
10 c.c. acetic acid, 20 percent.
5 amperes at 6 volts for 25 minutes.

The deposit is brilliant, and there is no precipitation on the anode.

61. Sodium formate is a very satisfactory electrolyte.[30]

Cobalt sulphate = 0.3535 g. metal.
2.5 g. sodium carbonate.
4 c.c. formic acid, 98 percent.

Heat to boiling, remove the flame and electrolyze with rotating anode at 5 amperes and 6 volts. Time, 30 minutes. The deposited cobalt is brilliant. A slight anode deposit may be removed by a few drops of a mixture of 5 c.c. glycerine, 45 c.c. alcohol, 50 c.c. water. A few drops of formic acid should be added from time to time to prevent the solution from becoming alkaline.

62. Lactic acid or a lactate makes an excellent electrolyte.[30] No precipitation occurs on the anode, and the cobalt deposit is exceedingly brilliant and adherent. A large excess of lactic acid retards precipitation.

2.2 g. sodium carbonate.
5 c.c. lactic acid, conc.
5 amperes at 8 volts precipitates 0.32 g. cobalt in 25 minutes.

63. Ammonium lactate is even superior to the preceding electrolyte.[30]

0.331 g. cobalt as sulphate.
30 c.c. ammonia.
7 c.c. lactic acid.
125 c.c. in volume.
6 amperes at 5 volts.
25 minutes is sufficient for complete precipitation.

64. Smith[30] uses a mercury cathode for the rapid determination of cobalt from its sulphate or chloride. At 4 amperes, 6 volts and 1,000 R. P. M. of anode, 0.35 g. of cobalt is precipitated in 15 minutes. It is necessary to add 10 c.c. of toluene or xylene to the chloride solution to prevent attack of the platinum anode.

65. Ammonium succinate can be employed, but some carbon is apt to be precipitated with the cobalt. Sodium succinate should not be used.

Separation of Cobalt and Nickel: Several solutions have been proposed for the difficult problem of separating cobalt and nickel by electrolysis.

66. Basse and Selva[31] add to the neutral or feebly acid solution of the metals an organic substance, such as tartaric or citric acid, glycerine, dextrose, etc., to prevent precipitation of the metals by excess of alkali; a large excess of caustic soda is added, and the solution is electrolyzed at a current of 0.3 to 1 ampere (per square decimeter?). Cobalt, iron and zinc are deposited, while nickel remains in solution. Ammonium carbonate is then added to the solution, and the nickel is deposited electrolytically.

67. G. Vortmann[32] adds to a neutral solution of the sulphates of the metals alkali or alkali-earth sulphates, and about 1 percent sodium chloride, and electrolyzes with frequent reversals of the current. Nickel remains in solution, and cobalt separates as hydroxide.

Neumann[29] (p. 215) says that this method is not suited to quantitative analysis.

68. Vortmann[29] also proposes to electrolyze solutions containing tartrates of the alkalies and a little potassium iodide. Neumann condemns this process also, and states that there is no reliable method for the electrolytic separation of cobalt and nickel.

Classen[27] (p. 241) ascribes to Vortmann the use of a solution containing sodium potassium tartrate, strongly alkaline by sodium hydroxide, but says that the essential data for repeating his experiments are lacking.

Bancroft[33] tested Vortmann's separation in an alkaline tartrate solution. He states that in this solution "the decomposition voltage of cobalt is about one volt lower than that of nickel." He finds that cobalt peroxide tends to precipitate at the anode, but this can be remedied by a high current density at the anode or by the addition of a few drops of concentrated nitric acid. In the latter case a little nickel peroxide may precipitate at the anode at low current densities. With a Classen dish as cathode and an E. M. F. of 1.9 to 2.0 volts between the electrodes, a good deposit of cobalt is obtained which gives no test for nickel, but some cobalt is always left in solution. If the voltage is raised to take out the last traces of cobalt, some nickel is also deposited. Heating the solution makes matters worse. The addition of potassium iodide, as recommended by Vortmann, is unsatisfactory. Addition of hydroxylamine sulphate, hydrogen peroxide, formaldehyde or sodium bisulphite helps a little, but does not remove the last traces of cobalt in a reasonable time. Nickel peroxide precipitates more readily the more carbonate and the less tartrate there is present, but, as cobalt peroxide tends to come down with the nickel peroxide, it is best to deposit nearly all the cobalt first, then to add sodium carbonate, and electrolyze with low current density at the anode. Proceeding in this way it was possible to separate one gram of cobalt from 0.1 g. nickel in eight days' electrolysis.

69. A. Coehn and E. Salomon[31] electrolyze neutral solutions of the sulphates or nitrates of cobalt and nickel, when the cobalt separates at the anode as peroxide.

70. A. Coehn, in a later patent,[35] by the addition of a persulphate to the former electrolyte, secures the precipitation of cobalt alone.

71. A. Coehn and E. Salomon,[36] to prevent cobalt and nickel from precipitating on the cathode when carrying out the above process, add to the solutions some metal more easily precipitated, *e. g.*, copper. In this case cobalt precipitates as peroxide on the anode, nickel remains in solution, and copper is deposited on the

cathode. Nitrate and sulphate solutions are well adapted to the process, which works better at elevated temperatures, e. g., 60° C. E. M. F. 1.5 to 2 volts. Current 0.1 ampere per square decimeter.

72. Perkin[28] (p. 170) says: "Many attempts have been made to separate cobalt and nickel electrolytically, but none of the methods so far published can be said to give very satisfactory results. The only method which can be at all recommended is that of A. Coehn and M. Glaser:[37] "The process depends upon the simultaneous deposition of the two metals—nickel at the cathode and cobalt at the anode. . . . The cobalt must be prevented from being precipitated on the cathode. Now, as hydrogen is only deposited 0.22 volt higher (lower?) than cobalt, too high an E. M. F. must not be employed, or else one must employ some method in which the deposition takes place at a lower potential than that at which the H ions are discharged, *e. g.*, the addition of a carbonate to the solution." To the neutral solution, containing not more than 0.1 g. cobalt, add 0.1 to 0.2 g. potassium dichromate and 3 to 4 g. potassium sulphate, make up to 500 c.c., and electrolyze at 0.10 to 0.15 ampere for 10 hours. E. M. F. 2.3 to 2.4 volts. All the nickel is deposited as metal at the cathode, and all the cobalt as peroxide at the anode. The peroxide is dissolved in acid, neutralized and precipitated as metal.

73. Balachowsky's method. Classen[27] gives:

0.3 g. of the metals in acetic acid solution.
3 g. ammonium sulphocyanide.
1 g. urea.

Ammonia to neutralize the free acid.

0.8 ampere per sq. decimeter, 1.0 volt, at 70 °to 80° C. Time, 1½ hours to precipitate the nickel. This contains sulphur, and should be dissolved in nitric acid, filtered and re-precipitated. The solution containing cobalt is boiled with nitric acid, filtered, and the cobalt deposited by any regular method.

Smith[30] (p. 266) uses:

10 g. ammonium sulphocyanide.
3 g. urea.
300 to 350 c.c. total volume.

After removal of the nickel the solution containing cobalt is

evaporated to dryness several times with nitric acid, and the residue taken up with water, before depositing the metal.

74. Method of Alvarez.[38] The salts of cobalt and nickel are dissolved in cold water, recently boiled, and saturated at 0° C. with sulphur dioxide, forming a yellow cobalto-cyanide, $Ni_2CO(CN)_6$, which becomes green after washing and drying. Dissolve 0.5 g. of this salt in 100 c.c. of water, add 40 c.c. of ammonia of sp. g. 0.927 and 5 g. of ammonium sulphate. Electrolyze at 4 amperes per square decimeter and 3.4 to 4 volts for 2 hours. A brilliant deposit of nickel is obtained, free from cobalt, but containing carbon.

At 50 to 60° C., 1 ampere at 3.8 volts, in one hour precipitates both metals from a solution of:

1 gram of $Ni_2Co(CN)_6$ in 100 c.c. water.
50 c.c. ammonia.
10 g. ammonium sulphate.

P. Brulylants[39] criticises the method as not detailed enough for successful use. He obtains both metals in the deposit and also in the residual solution.

Smith[30] obtained unsatisfactory results with this process.

To sum up, it appears that all electrolytic methods so far devised for separating cobalt and nickel fail in the hands of all save their inventors.

ELECTRODEPOSITION OF NICKEL.

The quotations which follow give the opinions of different authorities upon the nature of electro-deposited nickel, and some of the difficulties encountered in plating with this metal.

Langbein[5] (page 246) says: "Hot fats strongly attack nickel, while vinegar, beer, mustard, tea, and other infusions produce stains; hence the nickeling of culinary utensils or the use of nickel-plated sheet iron for that purpose cannot be recommended." Bouant[10] (page 186): "After having considered nickel as dangerous in the preparation of food, it is now recognized, on the contrary, to be harmless. Nothing prevents the extension of nickeling to utensils of copper, an operation doubtless more expensive than tinning, but giving much more durable results."

"To decrease the resistance of the nickel solutions, conducting salts are added to them, which are also partly decomposed by the current. . . . The use of sodium acetate, barium oxalate, ammonium nitrate, ammonium-alum, etc., we consider unsuitable, and partly injurious, and are of the opinion that with few exceptions potassium, sodium, ammonia, or magnesia, are best for bases of the conducting salts. The presence of a small amount of free acid effects without doubt the reduction of a whiter nickel than is the case with a neutral or alkaline solution. Hence a slightly acid reaction, due to the presence of citric acid, etc., with the exclusion of the strong acids of the metalloids can be highly recommended. . . . An alkaline reaction of nickel baths is absolutely detrimental."—Langbein.[5]

"Lowering of the acidity, and elevation of the temperature, current density and nickel content of the bath tend to produce a fine-grained and matte deposit. Addition of alkalies and salts of magnesium have a beneficial effect. Addition of ammonium salts hinder the production of thick deposits. . . . Deposits from chloride solutions are always crystalline and coarser grained than those from sulphate solutions. Their hardness is about the same. The observation that the deposit from a chloride solution deteriorates more readily than one from a sulphate solution is explained by the difference in fineness of grain. In the presence of magnesium sulphate, the deposit contains 0.2 to 0.4 percent magnesium. This deposit is no harder than ordinary nickel plate, but is very flexible and well suited to the production of electrotypes. A bath containing magnesium salts ought to be more acid than other baths, to prevent the deposition of oxide. A higher acid content explains the fact that nickel deposited from solutions containing ethyl-sulphuric acid are very hard. Sulphate solutions give more flexible deposits than chloride baths. Deposits from solutions containing sodium salts are especially flexible, probably because of their finer grain. Iron renders the nickel deposit very brittle."—K. Engermann.[40]

"A solution of chloride of nickel is used as electrolyte. By this method it is possible to prevent the contamination of electrolytic nickel with sulphur, as would be the case were a sulphate solution used as the electrolyte."[41]

In spite of the recommendation by various experimenters of

baths containing only nickel salts, there is a very general belief that for a successful nickel plating bath the salt of some other metal must be present, to form a double salt.

"Indeed it has been heretofore held as impracticable to nickel-plate with a single salt."—J. Yates.[37] "On the other hand, the simple acid salts of nickel have not hitherto been found to answer for the purpose of electrodeposition, from the fact that such solutions refuse to yield a reguline or cohesive deposit of metallic nickel."—J. Powell.[42]

Brass World[43] published a number of experiments with nickel sulphate solutions, made by an experienced practical plater to settle the question of whether or not single nickel salts can be used for plating. The conclusion is, "It is apparent, therefore, that single nickel salts cannot be used alone for plating."

The writer cannot subscribe to this result, for in 1904 he tried the deposition of nickel from a solution of 140 grams of commercial nickel sulphate per liter. Several trials gave black deposits, but finally a good deposit resulted. The solution was slightly diluted and 4 drops of sulphuric acid added. At the end of 38 hours electrolysis, with a current density of 5 amperes per square decimeter, falling to zero at the end, because of the complete solution of the anode, the deposit was excellent. Another trial of the same bath for 8 hours at 6 amperes per square decimeter gave a deposit of excellent appearance and firmly adherent. The current efficiency, however, was low.

Brochet[3] (page 229) says: "At the cathode the ion $Ni^{\cdot\cdot}$ ought to be discharged, and the metal pass into the molecular state and be deposited. In reality the reaction is much more complex, and the electrolysis of a pure salt of nickel generally gives poor results. With the sulphate there is the production of a slight black deposit, accompanied by an abundant evolution of hydrogen. With the chloride there is a deposit of nickel hydrate mixed with the oxychloride, and a similar evolution of hydrogen. A mixture of the sulphate and chloride of nickel gives much better results. The addition of an alkali-salt: potassium, sodium, ammonium, seems to be necessary to secure a good deposit; but then the series of reactions is entirely different. A complex salt is formed."

"It is a practice commonly adopted to momentarily use a high

E. M. F. until the work is just covered with nickel, and then to reduce the E. M. F.. This is called "striking," and 5 to 6 volts may for a few moments be used for this purpose. The E. M. F. is then quickly reduced to 2 or 3 volts."—Field.[44]

It is well known that there is greater difficulty in obtaining a satisfactory deposit of nickel on some metals than on others. Sackur[45] contends that: "A metal is more difficult to nickel, the farther its potential lies from that of nickel. Zinc, for example, possesses a higher electromotive force than brass, and this, in turn, more than iron. Potassium cyanide solution has a lower E. M. F. of decomposition than nickel chloride, and this again smaller than the sulphate. Good nickeling depends only on the choice of the right E. M. F., not upon the composition of the bath." This is an excellent illustration of the pitfalls of error which lurk within the covers of our electrochemical authorities—errors all the more insidious from the grain of truth in them.

One trouble, which was encountered in the earliest commercial nickel-plating, and it seems to have persisted to the present, in spite of the numerous remedies proposed, is the tendency of the deposit to peel off from the underlying metal.

In 1871 Keith[46] says: "The objection to nickel-plated goods thus far is that the deposit is so brittle that it cannot be bent, nor on many articles stand necessary wear even if not bent, and that it will also scale or peel off." In spite of the cure for this trouble announced by Keith, Peters[45] (page 153) writing in 1900, says: "When deposits of electrolytic nickel exceed a fraction of a millimeter in thickness they usually separate from the cathode in thin brittle leaves."

"The usual methods of electrolytically separating nickel from aqueous solutions of its salts do not permit of the production of deposits of more than one-hundredth of a millimeter in thickness, since with a longer continuance of nickeling the layer formed comes off in thin scales. This disadvantage can be avoided by using a heated electrolyte, as has been long known; but a thick nickel plate thus produced shows a crystalline structure as compared with the rolled nickel of commerce, is very brittle, and is therefore not suited for direct manufacture or technical utilization without being first melted over again."—M. Kugel.[20]

Turning from patentees, who may be regarded as prejudiced

witnesses, we find D. H. Browne,[47] saying: "The bug-bear encountered by all who attempt to produce sheets of nickel thicker than that used by nickel platers has been the tendency of nickel to crack and curl off in rolls, like wood shavings."

"Two of the difficulties which are often encountered in electroplating (with nickel) are either the formation of gray pulverulent deposits, or else the deposit does not adhere, but cracks and curls from the cathode. . . . The former difficulty has been found to be due to employing too high current density and too high E. M. F., whereas the latter difficulty is due to the electrolytes being too acid and at too low a temperature, or else to a film of grease or dirt on the cathode."—E. F. Kern.[48]

"Nickel well deposited is extremely hard, so hard that it cannot be burnished, and is somewhat brittle. Thick coatings are especially liable to flake off in use, unless exceptionally well deposited, and even the thinnest films will part from surfaces which are not chemically clean."—McMillan[4] (p. 217).

The cause of this brittleness and peeling of nickel deposits is indicated in the following quotations: "Using a neutral or ammoniacal solution of pure sulphate of nickel there is an abundant disengagement of gas from the anode; soon followed by an increasing production of hydrogen at the cathode, and the deposited nickel becomes detached, curling up like wood shavings."—M. Gresy.[49]

"The deposition of nickel requires a neutral bath. The presence of much free acid causes deposition of hydrogen, and the deposit of nickel in scales. Peeling of the nickel deposit is due to occlusion of hydrogen, which always exists in deposits of nickel and cobalt."—A. Brochet.[50]

"It is commonly considered that the curling up of electrolytic nickel plate is due to the co-deposited hydrogen."—Schoch.[51]

"The difficulty of obtaining thick nickel deposits is due to hydrogen evolved along with the metal and absorbed by it, causing brittleness."—A. Hollard.[52]

Another trouble occasionally referred to is the formation of pits on the surface of the deposit.

"The trouble you experience from dark and pitted deposits is due to occluded hydrogen. This trouble develops when the solution is low in metal and hydrogen gas forms very rapidly upon

the surface of the articles being plated. This gas theoretically burns holes in the deposit, causing the pitting noticed."[53]

"The occlusion of hydrogen tends to make the deposit somewhat brittle, and more or less porous, and hydrogen gas clings to the surface of the deposited metal in the form of very fine bubbles, thereby making the surface more or less warty and rough. . . . By maintaining in the bath a small amount of material which will combine with free hydrogen, *e. g.*, chlorine, the occlusion of hydrogen, etc., is prevented. . . . The chlorine may be introduced as a gas, by adding fresh bath saturated with chlorine, or in case of a chloride electrolyte by using a small insoluble anode to which a portion of the current is shunted. Free bromine may be used, but gives inferior results."—T. A. Edison.[54]

Photographs showing such pitting of iron[55] and nickel[56] deposits have been published.

The remedies most frequently proposed for the curling and brittleness of electrolytic deposits of nickel are strict neutrality of the bath, and electrolysis at high temperatures, varying between 30° and 100° C. H. J. Brownell[57] secures a deposit of nickel which will stand drawing, bending, spinning, etc., of the plated metal. "The article to be plated being heated by immersion in water or otherwise to a temperature of nearly 100° C. (212° F.), and then subjected to a hot nickel-plating bath." Foerster,[58] by heating from 50° to 90° C. an absolutely neutral bath containing 140 g. nickel sulphate per liter, obtained deposits 0.5 to 1.0 mm. in thickness. The current density was 2 to 2.5 amperes per dm.^{2} Other methods of preventing the curling of nickel, depending on the addition of particular substances to the electrolyte, will be mentioned later.

Purity of Nickel Anodes.

Calhane and Gammage,[59] analyzed commercial anodes from two different establishments and found 7.57 and 7.52 percent iron in them, and 92 percent nickel. Using these anodes, the deposit always contained iron, varying in amount between 0.07 and 0.75 percent.

The following is a formula given for the making of nickel anodes:[60] 92 parts nickel, 4 parts tin, 4 parts old files.

O. W. Brown[61] finds copper present in a nickel anode: "The presence of the copper, rather than being a detriment, seems to be advantageous in allowing a high anode current density to be used.

"Commercial nickel anodes contain, in addition to nickel, iron, tin and carbon. These are introduced intentionally to render the anode 'soft,' *i. e.,* so that it will dissolve easily in the solution during plating."[62]

Since such anodes are largely used in this country it is evident that much of the nickel plate produced here contains a small amount of iron. It is to this iron that Bancroft[63] ascribes the ready rusting of nickel-plated objects when exposed to the weather: ". . . All our nickel plate contains iron. I am confirmed in that belief by the fact that the nickel-plating on the Weston instruments, which I assume to be as good as any that would be put on the market, rusts red in the laboratory. I take it that this is due to iron in the nickel plate. . . . If a bicycle is left out over night it will rust." The writer does not regard the above allegations as proved until rust has formed on such nickel plate deposited on copper or some other surface which is in itself entirely free from iron.

Passivity of Nickel Anodes.

It has long been known that rolled nickel anodes do not dissolve satisfactorily in the standard plating solution, nickel ammonium sulphate. This phenomenon was brought to the attention of this Society by O. W. Brown.[64] Brochet[3] (page 228) says: "Nickel is a passive metal, that is to say that to a certain degree and under certain conditions it dissolves incompletely and acts as a noble metal—as an insoluble anode. Sulphuric acid is then formed at the anode, and nickel dissolves in an amount less than that required by Faraday's law." Speaking of nickel anodes, McMillan[4] (page 222) says: "Nickel anodes must be as pure as it is possible to obtain them. They are to be had cast or rolled. Cast anodes being the more readily soluble are more likely to neutralize the acid set free by electrolysis at the anode, and hence the natural tendency of the (ammoniacal) nickel bath to become alkaline asserts itself. Rolled anodes are more likely, by insufficiently neutralizing the acid, to cause the bath to become

acid." Bancroft[63] points out that a pure nickel anode may be made to corrode satisfactorily in nickel ammonium sulphate by adding to the solution a small percentage of nickel chloride or ammonium chloride. He recommends the use of anodes of pure nickel and the complete elimination of iron from the nickel bath. Brochet[65] says: "The greater or less passivity of the anode depends on the physical nature of the metal, *i. e.*, the hammering or rolling to which it has been subjected, not on its purity."

On the contrary, Kern[48] says: "Another cause of gassing is the use of pure metal anodes in nickel-ammonium sulphate electrolyte, as the pure metal does not readily dissolve. However, pure nickel anodes may be successfully used in this electrolyte if a small amount of chloride salt is added, the presence of which causes the anode current efficiency to approximate 100 percent." Langbein[5] (pages 247 and 254) objects to the addition of chlorides or nitrates to baths for nickeling iron: "Iron objects nickeled in such a bath come out faultless, but in a short time, even if stored in a dry place, portions of the nickel layer will be observed to peel off, and by closely examining them it will be seen that under the deposit a layer of rust has formed which actually tears the nickel off." E. Weston[66] says: "It has been found that the solution of the double chloride of nickel and ammonium is better adapted for coating iron with nickel than the double sulphate solution, the latter answering better for brass."

In the electrolytic refining of iron the writer found that deposits from a chloride electrolyte rusted very much worse than those obtained from a solution containing only sulphates.

NICKEL PLATING BATHS.

For convenience the baths will be classified as follows:

I. Baths containing single salts of nickel.
II. Baths containing double salts.
III. Miscellaneous baths.
IV. Baths for deposition of malleable nickel.
V. Baths producing thick deposits.
VI. Agents for the production of smooth deposits.
VII. Nickel electrotypes.
VIII. The nickeling of zinc.

I. Baths Containing Single Salts of Nickel.

a. Neutral Baths:

Under this title will be grouped the baths formed by simple solution of the nickel salt without rendering it distinctly acid or alkaline, as well as those baths whose neutrality is specifically stated.

75. Yates' acetate solution.[67] Nickel acetate is dissolved in water to a strength of 8° or 10° Bé. (1.058 to 1.074 sp. g.). It is claimed to have the advantage over other solutions of a larger proportion of metal of not being subject to the irregular decompositions which render the continued operation of other baths so difficult, and to permit of direct nickeling on metals which it has heretofore been impracticable to nickel without a previous coating of copper. Plate steel, cast and wrought iron are mentioned as examples of this. With care, zinc may also be nickeled directly in this bath.

In referring to the fifty different nickel baths tried by Alexander Watt,[68] a number placed in parenthesis after the title of the bath indicates the numbering in his paper.

76. Watt's acetate bath (1). This consisted of 120 grams of neutral nickel acetate per liter. At a current density of 2.4 amperes per square decimeter a uniform but somewhat dark deposit was obtained. At the end of an hour's deposition a steel burnisher was applied, which brightened the surface, showing that the metal was softer than that obtained from the ordinary double sulphate solution.

77. Watt's[68] nickel benzoate solution (46). This solution yields a bright deposit, soft enough to be burnished.

78. Watt's[68] nickel borate solution (48). This yields a white deposit.

79. Nickel chloride solution[68] (22). 15 grams of nickel chloride per liter gave a brisk evolution of hydrogen and a deposit of metal not quite so white nor so fully adherent as the deposit from the double sulphate.

80. Nickel citrate solution[68] (6). This was prepared like most of the other salts of this set of experiments, by digesting moist nickel carbonate with a hot solution of the acid. The first

deposit was not of satisfactory whiteness, but this was improved by increasing the current.

81. Nickel lactate[68] (12). This salt is readily soluble, and gives a deposit of fairly good color.

82. Nickel nitrate[68] (16). Nickel carbonate was dissolved in nitric acid diluted with two volumes of water until a neutral solution was obtained. Neither a deposit of metal nor of hydrogen was obtained with one, two or even three Daniell cells in series. There was a slight evolution of oxygen at the anode.

83. J. Mathieu's propionate solution.[69] He used a solution of nickel propionate of about 5° Bé. (sp. g. 1.0357). No results are stated, nor are any claims made in regard to the superlative excellence of the product.

84. Nickel salicylate[68] (47). This gives a white deposit.

85. Nickel sulphate[68] (18). A solution was made by dissolving 100 grams of the crystals per liter of water. The deposit was of good color, but was not so adherent as deposits from the double sulphate of nickel and ammonia.

86. Nickel sulphate, neutralized by lime or calcium carbonate.[70] To 100 parts of an acid aqueous solution of nickel sulphate he adds 3.75 to 7.5 parts of hydrate of lime to exactly neutralize the acidity of the sulphate. To avoid the danger of an excess of alkali he prefers, however, to neutralize by the carbonate of lime. "This solution produces a brighter metallic deposit than the solution in general use, and without the addition of ammonia in any form."

87. Nickel sulphocyanide[68] (20). Moist nickel carbonate was dissolved in a strong solution of potassium sulphocyanide, and this was electrolyzed with the current from three cells. A dark steel-gray deposit was immediately formed, which did not alter during a half hour's deposition. Gas was evolved at both electrodes.

88. Nickel tartrate[68] (11). The solution prepared by digesting moist nickel carbonate in a strong, hot solution of tartaric acid is a poor conductor, and three cells in series were required to produce a deposit of an indifferent color. It was noticed that the cathode became more fully coated with metal on the back than on the front.

b. Acid Baths:

89. Nickel acetate.[71] The solution contains about 60 grams of nickel acetate per liter, and is maintained strongly acid by acetic acid. "These solutions thus prepared and used do not become depleted in using, and require no addition of nickel to keep up their strength other than that derived from the nickel of the anode."

90. Nickel citrate[68] (26). The solution was prepared by electrolyzing a strong solution of citric acid with a nickel anode. The deposit was very bright, of a good white color, much softer than is usual with nickel, and received a high polish under the steel burnisher.

91. Nickel formate.[72] The solution contains nickel formate with excess of formic acid. Among its claims to merit are: "The solution needs no replenishing with salts of nickel, the nickel being supplied from the anode. No precautions need be taken to see that the solution is free from the presence of potash, soda, alumina, lime or nitric or other acid. The deposit may be of any thickness, and will always be firm, flexible and white."

c. Alkaline Baths:

92. Nickel ammonio-acetate[68] (32). Ammonia was added to a strong solution of nickel acetate until the liquid acquired a deep blue color. The deposit was bright, of a good color and very adherent.

93. Nickel ammonio-carbonate[68] (35). Nickel carbonate was dissolved in strong ammonia, diluted and electrolyzed. The deposit was white, and retained its original brightness after an hour's deposition.

94. Nickel carbonate[68] dissolved in a strong solution of ammonium carbonate gave a rather dark deposit.

95. Nickel ammonio-chloride[68] (30). Strong ammonia was added to a solution of nickel chloride until the solution acquired a deep blue color. The deposit was white and very bright. Very little hydrogen, but much oxygen was evolved.

96. Nickel ammonio-citrate[68] (33). Ammonia was added to a strong solution of nickel citrate. The deposit was white, bright

and very adherent. The anode kept perfectly clean during the electrolytic action.

97. Nickel ammonio-ferricyanide[68] (45). Nickel ferricyanide was dissolved in strong ammonia. The filtered and diluted solution gave a prompt and fairly white deposit on brass.

98. Nickel hydroxide in ammonia[68] (15). This solution gave a yellowish deposit of nickel, without hydrogen. Oxygen was abundantly evolved at the anode, which became coated with a brownish film.

99. Nickel ammonio-nitrate[68] (31). Excess of strong ammonia was added to a solution of nickel nitrate. The nickel deposit was rather dark in color, and after a half hour the anode had a deep brown color.

100. Nickel ammonio-sulphate[68] (19). An experiment was tried to ascertain the effect of small and increasing additions of ammonia to the sulphate solution. The current from three cells was used, and a fresh brass cathode was used after each addition of ammonia. After the first addition of ammonia the deposit appeared much brighter than that obtained from nickel sulphate alone, and this characteristic was maintained until the solution acquired a deep blue color. The anode was almost black, and a flocculent precipitate formed in the solution.

The evolution of oxygen or the formation of nickel oxide on the anode, mentioned in many cases, indicates that those particular baths are not suited to practical use because of poor corrosion of the anode. In only one case, No. 96, is there mention of good anode corrosion in these alkaline baths.

II. Baths Containing Double Salts.

In connection with these baths it will be of interest to review the patents of Adams under which for many years nickel plating was monopolized. His first U. S. Patent, 93,157, of Aug. 3, 1869, claims:

"1. The electrodeposition of nickel by means of a solution of the double sulphate of nickel and ammonia, or a solution of the double chloride of nickel and ammonium, prepared and used in such a manner as to be free from the presence of potash, soda, alumina, lime, or nitric acid, or from any acid or alkaline reaction."

"2. The use, for the anode of a depositing cell, of nickel combined with iron to prevent the copper and arsenic which may be present from being deposited with the nickel or from injuring the solution."

"3. The electroplating of metals with a coating of compact, coherent, tenacious, flexible nickel of sufficient thickness to protect the metal upon which the deposit is made from the corrosive agents with which the article may be brought in contact."

"4. The deposition of electrotype-plates of nickel to be removed from the surface on which the deposit is made and used separately therefrom."

It is easy to see how it was possible to monopolize nickel plating under this unjust patent. Even today manufacturers of anodes have not recovered from its baneful influence, but are still furnishing anodes in accordance with claim No. 2, to the great detriment of the nickel plating industry.

Adams' patent, 100,961, March 22, 1870, is remarkable for its contradictory claims. "This improvement consists in the use of three new solutions from which to deposit nickel by the electric current: First, a solution formed of the double sulphate of nickel and alumina, or the sulphate of nickel dissolved in a solution of soda, potash, or ammonia alum, the three different varieties of commercial alum; Second, a solution formed of the double sulphate of nickel and potash; Third, a solution formed of the double sulphate of nickel and magnesia, *with* or without *excess* of *ammonia*. . . . I prefer to use these solutions at a temperature above 100° F. (38° C.), but do not limit my invention to the use of these solutions at that temperature. I therefore claim:

"1. The electrodeposition of nickel by means of a solution of the double sulphate of nickel and alumina, prepared and used in such a manner as to be free from the presence of ammonia, potash, soda, lime or nitric acid, or from any acid or alkaline reaction."

"2, . . . A solution of the double sulphate of nickel and potash, prepared and used in such a manner as to be free from the presence of ammonia, soda, lime, or nitric acid, or from any acid or alkaline reaction."

"3. . . . A solution of the double sulphate of nickel and magnesia, prepared and used in such a manner as to be free from the presence of potash, soda, alumina, lime or nitric acid, or from any acid or alkaline reaction."

In U. S. Patent 136,634, March 11, 1873, Adams' claim was still further extended. "I now claim . . . The electrodeposition of nickel, or the electroplating with nickel, by means of a solution of either of the soluble salts of nickel, such solution being prepared and being used, substantially, free from the presence of potash, soda, lime, alumina, and nitric acid, or either of them, and free from acid and alkaline reaction, or from either."

a. Neutral Baths:

In this class will be included baths made by merely dissolving normal salts, as well as those solutions which have been carefully neutralized.

The bath most generally used is a solution of nickel ammonium sulphate.

101. Pfanhauser's solution[73] (page 361). 75 grams of nickel ammonium sulphate per liter. Current density, 0.3 ampere per dm.^{2} Temperature 15 to 20° C. Resistivity 24.6 ohms. 3.5 volts for 15 cm. between electrodes. Temperature coefficient 0.0176 for 1° C. Specific gravity 1.047. Current yield 91.5 percent. Deposit per hour 0.0034 mm. Cast anodes of ½ to ¾ the area of cathode should be used. The deposit is hard, good for plating iron or steel. Langbein[5] says the cast anodes rapidly render the bath alkaline, necessitating a frequent correction of the reaction. Brochet[3] (page 237) says: "This bath is poor in metal, even in case of the saturated solutions (98 grams at 18° C.). It is better to replace a part of the double sulphate by the single sulphate." He recommends:

102. Solution of single and double sulphates:[3]

Nickel sulphate	166 grams.
Nickel ammonium sulphate	55 grams.

Specific gravity 1.101, resistivity 23.9, at 18° C., nickel per liter 39 grams. "Baths rich in metal possess the advantage of greater covering power and are less influenced by cold. The addition of ammonium sulphate is sometimes recommended to

increase the conductivity of the bath; this should not be done, since it results in the impoverishment of the bath in metal." —Brochet.[3]

103. The double sulphate with ammonium sulphate:[5]

Nickel ammonium sulphate....	50 grams
Ammonium sulphate	50 grams

"E. M. F. at 10 cm. 1.8 to 2 volts. Current density 0.35 ampere. The bath deposits rapidly, and all metals (zinc, lead, tin, and Britannia, after previous coppering) can be nickeled in it. Upon rough castings and iron, a pure white deposit is difficult to obtain. On account of the great content of ammonium sulphate in the bath, the deposit piles up, especially on the lower portions of the objects, which readily become dull, while the upper portions are not sufficiently nickeled."—Langbein.[5]

104. Pfanhauser[73] gives:

Nickel sulphate	50 grams
Ammonium chloride	25 grams

Specific gravity 1.0357 (5° Bé.). Resistivity 17.6 ohms. Temperature coefficent 0.025. E. M. F. for 15 cm. 2.3 volts. Current density 0.5 ampere. Current yield 95.5 percent. Deposit per hour 0.0059 mm. Cast anodes half the area of cathode. Langbein[5] gives 57 grams and 29 grams, respectively, of the same salts, and states that the deposit is soft and white, that heavy deposits cannot be obtained because of the danger of peeling, and that the bath is not suited to the direct nickeling of iron.

105. Bath with magnesium sulphate:[5]

Nickel ammonium sulphate ..	56 grams.
Magnesium sulphate	26 grams.

"E. M. F. 4 volts at 10 cm. Current density 0.2 ampere. Good for plating on iron, and may be used for the direct nickeling of zinc. The deposit is soft, and of a yellowish tinge. The bath does not remain constant, but fails after working three or four months, even cast anodes being but little attacked."—Langbein.[5]

Watt experimented with a solution containing the sulphates of nickel and magnesium. At first the deposit was decidedly yellow

in tone, but became whiter after a few hours' use of the solution.

Adams' patent of the double sulphate of magnesium and nickel has already been noticed.

106. To a solution of nickel ammonium sulphate Watt[68] gradually added a concentrated solution of ammonium citrate. A bright deposit of a slightly yellowish tone was obtained, which retained its brightness during deposition for a long time, but finally became dull. The deposit was soft enough to be burnished. There was a brisk evolution of gas at the anode, and a few bubbles of hydrogen clung to the cathode.

107. Langbein[5] gives a somewhat similar bath, as do C. H. Procter[74] and Pfanhauser:[73]

	Langbein	Procter	Pfanhauser
Nickel sulphate	26.0 grams	30 grams	40 grams
Ammonium chloride	17.5 "	30 "	0 "
Potassium citrate	17.5 "	18 "	35* "

* Sodium citrate.

Langbein specifies for copper and copper alloys: Current density 0.45 to 0.5 ampere, E. M. F. at 10 cm. 1.5 to 1.7 volts. For zinc, current density 0.8 to 1 ampere, E. M. F. 2 to 2.5 volts.

Pfanhauser gives a current density of 0.27 ampere, E. M. F. at 15 cm. 3.6 volts. Specific gravity 1.039 (5½° Bé.). Resistivity 51.7 ohms. Temperature coefficient 0.0348. Current yield 90 percent. Deposit per hour 0.00301 mm. Rolled anodes. The bath yields a soft white deposit, and is especially suited for plating pointed objects like knives.

108. An English solution:[16]

Nickel ammonium sulphate	100 grams.
Ammonium acetate	50 grams.

109. Another English solution:[16]

Nickel ammonium acetate	100 grams.
Ammonium chloride	20 grams.
Glycerine	5 grams.

110. Nickel and ammonium chlorides:[5]

Nickel chloride, cryst.	37.5 grams.
Ammonium chloride	37.5 grams.

The bath is neutralized by ammonia. E. M. F. at 10 cm. 1.75 to

2 volts; for zinc, 2.8 to 3 volts. Current density 0.5 ampere. "The bath deposits readily, and is especially liked for nickeling zinc castings."

111. H. P. Dechert's solution:[75]

Nickel chloride, cryst. at least	141 grams.
Calcium chloride solution of 30° Bé. (sp. g. 1.261)	1 liter.

The advantages claimed for this solution are very low resistance, elimination of hydrogen bubbles from the surface to be plated, thus removing the danger of spotting, a permanent and enduring solution, and a smooth, close and tough deposit of nickel.

112. Watt[68] gradually added to a solution of nickel sulphate a solution of ammonium tartrate, and obtained a very bright and very white deposit of nickel.

b. Acid Baths:

E. Weston[66] in his patent claims: "1. The electrodeposition of nickel by means of solutions of the salts of nickel containing boric acid, either in its free or combined state."

"2. A solution of the single or double salts of nickel to which has been added boric acid, either in its free or combined state." The exact composition of the baths is not stated by Weston. He claims that the addition of boric acid or its compounds prevents the deposition of sub-salts upon the cathode, renders the solution more constant and stable in composition, diminishes the liability to the evolution of hydrogen, permits the use of a more intense current, and improves the character of the deposit by rendering it less brittle and by increasing the tenacity with which it will adhere to a metal surface.

Langbein[5] (page 249) says: "Boric acid, recommended by Weston as an addition to nickeling baths, has a favorable effect upon the pure white reduction of the nickel, especially in nickeling rough castings. . . . Numerous experiments have shown that the deposit of nickel from nickel solutions containing boric acid is neither more adherent nor softer and more flexible than that from a solution containing small quantities of a free organic acid. Just the reverse, the deposit is harder and more brittle in the presence of boric acid.

"Weston recommends the following composition for baths:[5]

"113. Nickel chloride ..... 26 grams.
Boric acid ..... 10.5 grams.

"114. Nickel ammonium sulphate.. 38 grams.
Boric acid ..... 19 grams.

"Both solutions are said to be improved by adding caustic potash or caustic soda so long as the precipitate formed dissolved. These compositions, however, cannot be recommended, because the baths work faultlessly for a comparatively short time only."

115. Pfanhauser[73] gives:

Nickel ammonium sulphate.. 40 grams.
Ammonium chloride ..... 15 grams.
Boric acid ..... 20 grams.

Current density 0.5 ampere. E. M. F. for 15 cm. 2.8 volts. Resistivity 20.85 ohms at 15° to 20° C. Temperature coefficient 0.0156. Current yield 89.5 percent. Deposit per hour 0.00556 mm. Specific gravity 1.0357 (5° Bé.). He, too, speaks of the difficulty of regulating the bath, and recommends cast anodes of half the surface of the cathode.

Maigne and Mathey[16] ascribe to Weston the two baths which follow:

116. Nickel chloride ..... 50 grams.
Boric acid ..... 20 grams.

117. Nickel sulphate ..... 50 grams.
Boric acid ..... 17 grams.

118. Bath of Julius Weiss:[16]

Nickel sulphate ..... 40 grams.
Ammonium chloride ..... 20 grams.
Citric acid ..... 2 grams.

119. Langbein[5] (p. 253) gives:

Nickel ammonium sulphate.. 64 grams.
Ammonium sulphate ..... 20 grams.
Citric acid ..... 4.4 grams.

E. M. F. 2 to 2.2 volts at 10 cm. Current density 0.34 ampere. The materials are dissolved in boiling water, and ammonia is

added until blue litmus paper is only slightly reddened. Very careful regulation of the current is required to avoid peeling off. The anodes should be cast and rolled in equal numbers. According to experiments by Dr. Langbein it is better to decrease the amount of ammonium sulphate to 2 grams.

This bath is operated so nearly neutral that it closely resembles bath No. 107.

120. J. H. Potts[76] uses:

Nickel acetate	28 grams.
Calcium acetate	16 grams.
Acetic acid, sp. g. 1.047 (35 percent)	8 grams.

Potts claims: "I have succeeded in producing a nickel-plating solution having the advantages of the presence of free acid and of great density, and yet free from the objections which have been heretofore made to acid solutions. . . . To the presence of the acetate of lime I also attribute the fact, which I have discovered in practice, that in the use of my solution no such care and nicety in the regulation of the electric current are necessary as in the use of the ordinary solutions. . . . Another advantage of my solution is the entire freedom of iron work plated in it from liability to corrosion after removal from the the cleansing bath of warm water in which it is necessary to place it after leaving the plating solution, thus obviating a very serious objection heretofore made to the presence of free acid in a nickel-plating solution—an objection which has been found to exist in the use of ordinary solutions." Watt[11] (p. 297) quotes Wahl as follows: "It gives satisfactory results without that care and nicety in respect to the condition of the solution and the regulation of the current which are necessary with the double sulphate solution. The metallic strength of the solution is fully maintained without requiring the addition of fresh salt, the only point to be observed being the necessity of adding from time to time (say once a week) a sufficient quantity of acetic acid to maintain a distinctly acid reaction. It is rather more sensitive to the presence of a large quantity of free acid than to the opposite condition, as in the former condition it is apt to produce a black deposit, while it may run down nearly to neutrality

without notably affecting the character of the work. The deposited metal is characteristically bright on bright surfaces, requiring but little buffing to finish. It does not appear, however, to be so well adapted for obtaining deposits of extra thickness as the commonly used double sulphate of nickel and ammonium. On the other hand, its stability in use, the variety of conditions under which it will work satisfactorily and the trifling care and attention it calls for make it a useful solution for nickeling."

121. "W. Baker and J. Unwin[77] dissolve nickel hydrate in tartaric acid and add potassium hydrate or ammonia nearly to neutralization, so that a double salt is formed."[17]

122. Placet and Bonnet's nickel solution, see bath No. 25, this paper.

123. For Nagel's nickel solution see bath No. 7.

124. For Kugel's nickel solution see No. 23.

c. Alkaline Baths:

125. Roseleur's solution:[16]

Nickel ammonium sulphate ..	40 grams.
Ammonium carbonate	30 grams.

126. Desmur's solution:[11]

Nickel ammonium sulphate ..	70 grams.
Sodium bicarbonate	8 grams.

The bath is worked nearly at the boiling point. If, after working for some time, the deposit becomes dark, a small lump of sodium sulphide will remedy it. "Of all the solutions of nickel which I have tried," says M. Desmur, "this has, without doubt, given me the best results both as to quickness of working and whiteness of deposit, which is equal to that of silver. Nickel deposited from this solution can be burnished."

121. Bischof and Thiermann's[78] solution:

Nickel sulphate	86 grams.
Ammonium sulphate	67 grams.
Ammonia, sp. g. 0.905.....	110 grams.
Volume	1 liter.

Platinum anode. E. M. F. 2.8 volts. Current density 0.5 ampere.

128. Prior's solution.[79] He adds to nickel chloride solution ammonium chloride, sodium chloride and potassium hydrate until the solution is strongly alkaline.

129. Gutensohn's solution.[80] He claims to deposit nickel, aluminum, copper, lead and zinc from a solution of the phosphate of the desired metal dissolved in a solution of sodium hydrate to which ammonia is added.

130. F. Weil[81] dissolves nickel hydroxide in Seignette's salt and sodium hydrate.

III. Miscellaneous Baths.

Although even traces of nitrates are declared by Adams to be harmful in the nickel bath, several solutions have been used or patented in which a nitrate is the principal or an important ingredient.

131. Boden's solution:[16]

Nickel nitrate	27 grams.
Sodium sulphite	333 grams.
Ammonia	27 grams.

132. George Brucker[82] patents a solution composed of:

100 parts saturated solution of nickel in nitric acid.
3 parts cream of tartar.

133. Watt[68] (17) added ammonium nitrate to a neutral solution of nickel nitrate but obtained only a slight discoloration of the cathode. No hydrogen was liberated, but small bubbles of gas appeared at the anode.

134. Watt[68] (43) also tried the addition of ammonium citrate to the solution of nickel nitrate, but without any favorable action.

The double cyanide solution, used for the deposition of so many of the metals, in the case of nickel is conspicuous by its absence from all save two of the books on electroplating so far referred to in this paper. Watt[11] says, page 298: "This was one of the earliest solutions used for depositing nickel, and is capable of yielding an exceedingly white deposit. Though neither so economical nor so susceptible of yielding stout deposits of nickel as the ordinary double sulphate or double chloride, it may

be advantageously employed when only a thin coating of a fine white color is desired. It is stated to be somewhat extensively used in some large nickel-plating works in the United States." Nickel cyanide is dissolved in a strong solution of potassium cyanide and a small excess of the latter is added. "The solution should be as concentrated as possible, almost to the point of saturation."

135. Thomas and Tilley[83] in 1854 patented a nickel bath consisting of a solution in potassium cyanide of the washed precipitate from a solution of nickel in nitric acid.

Watt[68] failed to get a deposit of nickel in the three experiments which follow:

"A solution was prepared by digesting recently precipitated phosphate of nickel in a moderately strong solution of cyanide of potassium. With the current from three cells, no metallic deposit was obtained, but a red salt formed at the cathode. A deposit of a black color appeared on the anode. There was a copious evolution of gas at both electrodes."

"A solution was prepared by adding recently precipitated and moist carbonate of nickel to a strong solution of cyanide of potassium. . . . There was much hydrogen given off, and the solution failing to yield a good film was abandoned."

"To a strong solution of cyanide of potassium moist ferricyanide of nickel was added. . . . No deposit of nickel could be obtained even when the cathode was briskly agitated in the bath. There was a brisk evolution of gas at both electrodes."

It looks like a case of too much free cyanide in the above solutions.

136. Bates[84] black nickel solution:

"Nickel salts"	120 grams
Cyanide of potassium	75 grams
Ammonia	108 grams
Water	1,000 grams

The nickel salts are dissolved in water, the cyanide added with stirring until the precipitate formed is dissolved, then the ammonia added—which should turn the solution to a light blue color. Nickel anodes are used. "The object of my invention is

the electrodeposition of a black nickel which shall be as compact, coherent, tenacious, and flexible as the best deposit of white nickel."

Many "black nickel" solutions contain sulpho-cyanides, compounds of arsenic, antimony, or other substances whose presence in other baths, containing no nickel, causes a deposit similar to "black nickel." Until proved by analysis, the writer doubts that "black nickel" is either nickel or one of its compounds. Hence modern "black nickel" solutions are not included in this paper.

137. Adams' sulphite solution:[85]

Nickel sulphate	37.5 grams.
Ammonium sulphite or bisulphite	22.5 grams.

"The resulting products are sulphite of nickel and sulphite of ammonia, and a residuary product of sulphate of ammonia. This solution may also be made from the nitrate, chloride, or acetate of nickel by adding the proper quantity of sulphite or bisulphite of ammonia. It may be used with special advantage where the nickel plate forming the anode in the solution contains zinc. Nearly all commercial nickel contains more or less zinc, the presence of which tends to increase the evolution of hydrogen on the deposited plate. There is less tendency to this evolution of hydrogen with this solution than with those heretofore described in books."

138. Langbein[5] gives a phosphate solution:

Nickel phosphate	19 grams.
Sodium pyrophosphate	80 grams.

E. M. F. at 10 cm. for copper 3.5, for zinc 3.8 volts. Current density for copper 0.5, for zinc 0.55 ampere. "The bath yields a very fine dark nickeling upon iron, brass, and copper, as well as directly, without previous coppering, upon sheet zinc and zinc castings. For the same purpose a nickel solution compounded with a large quantity of ammonia has been recommended. However, experiments with this solution always yielded lighter tones than the above bath."

139. Powell's pyrophosphate solution:[86]

Nickel phosphate	22.5 grams.
Sodium pyrophosphate	26.2 grams.
Nickel citrate	15. grams.
Sodium bisulphite	7.5 grams.
Ammonia, 16 percent	37.5 grams.

"One great advantage arising from the use of my solutions is that the various metals and their alloys are electronegative to a solution containing pyrophosphates or phosphoric acid; hence, no decomposition or local action occurs when they are immersed in the bath. Thus zinc articles, which cannot be plated in a solution of double sulphate or chloride of nickel and ammonia, are beautifully plated with a firm adhesive layer of metal by using my solutions, and the deposit is white in color and very ductile."

140. Nickel fluosilicate:[87]

Nickel fluosilicate	100 grams.
Aluminum fluosilicate	50 grams.
Ammonium fluoride	50 grams.

The deposit is claimed to be smooth, dense, coherent, and adherent. It is advisable to add ammonium fluoride from time to time during use to prevent the separation of silica.

141. A bath with sodium chloride:[3]

Nickel sulphate	50 grams.
Nickel ammonium sulphate	50 grams.
Sodium chloride	10 grams.

Sp. gravity 1.064 (8½ Bé.). Resistivity 23.4 ohms. Nickel per liter 18 grams. "The addition of 10 to 15 grams of boric acid per liter preserves the whiteness of the nickel deposit, which the presence of the chloride tends to make it lose."

Organic salts and compounds have been largely used, either as the basis of the bath, or as an addition for the purpose of improving the permanency of the bath or the nature of the deposit.

142. Watt[68] added sodium chloride to a strong solution of

nickel acetate, and with two cells obtained a good white deposit of nickel on brass.

143. To a strong neutral solution of nickel acetate Watt[68] added potassium acetate. The deposit of nickel was very uniform and white. There was only a moderate evolution of gas at the anode, and none at all on the cathode.

144. To a solution of nickel sulphate Watt[68] added a solution of nickel acetate. The deposit was bright, very white, and brightened under the burnisher without excessive pressure.

For other acetate baths see solutions 75, 76, 89, 92, 108 and 109.

Citric acid and citrates are frequently used in the nickel bath.

145. Pfanhauser[73] gives:

Nickel sulphate	40 grams.
Sodium citrate	35 grams.

E. M. F. at 15 cm. 3.6 volts. Current density 0.27 ampere. Specific gravity 1.0394 or 5½° Bé. Resistivity 51.7. Temperature coefficient 0.0348. Current yield 90 percent. Deposit in one hour 0.00301 mm. Rolled anodes should be used of twice the cathode surface. This bath is equally good for nickeling iron, steel and brass, and is especially good for nickeling pointed objects. The deposit is white and ductile.

146. Langbein[5] gives a similar bath:

Nickel sulphate	48 grams.
Sodium citrate	30 grams.

"E. M. F. at 10 cm. 3.0 volts. Current density 0.33 ampere. This bath is claimed to be especially useful in preparing nickel electrotypes, but Langbein's experiments proved it to possess the disadvantages of all nickel baths prepared with large quantities of organic salts. For the special purpose for which it is recommended no better results were obtained than with any other nickel bath rationally composed for heavy deposits. It is very suitable for nickeling objects with sharp edges and points. The deposit is quite soft, and in grinding such nickeled instruments, peeling off of the nickel happens less frequently than with instruments nickeled in other baths."

147. Watt[68] added citrate of ammonia to a solution of citrate of nickel. Three cells caused a somewhat dull deposit, but on diluting the solution the color and brightness of the deposit were much improved. The deposit was readily brightened by the burnisher. The anode was covered with a greenish coating, which dissolved on standing at rest in the solution. Addition of a slight excess of citric acid kept the anode clean.

148. J. E. Chaster[88] patents a bath consisting of a solution of nickel ammonium citrate. It is to be used about three-fourths saturated. Its particular advantage over the double sulphate is claimed to be its lower E. M. F. of decomposition.

149. Watt[68] also tried the effect on the deposit of continued additions of nickel citrate to a solution of nickel sulphate. Even a small addition of the citrate caused a whiter deposit than that from the sulphate and a larger amount caused the deposit to continue bright, instead of becoming dull after a short deposition as it usually does in a solution of nickel sulphate. The metal felt soft under the burnisher, and a brilliant polish was obtained.

For other citrate baths see solutions 80, 90, 96 and 107.

Jas. Powell[89] patents the addition of benzoic acid or benzoates to any of the salts of nickel, claiming that it renders the solution more stable, causes proper corrosion of the anodes and yields a tough, cohesive and reguline deposit of beautiful silvery-white nickel. As an example of his solution he cites:

150.	Nickel sulphate	34 grams.
	Nickel citrate	15 grams.
	Nickel phosphate	15 grams.
	Benzoic acid	7.5 grams.

The four solutions which follow are also ascribed to Powell:[16]

151.	Nickel sulphate	27 grams.
	Nickel citrate	20 grams.
	Benzoic acid	6.5 grams.

152.	Nickel chloride	14 grams.
	Nickel citrate	14 grams.
	Nickel acetate	14 grams.
	Nickel phosphate	14 grams.
	Benzoic acid	7 grams.

153. Nickel sulphate ..... 20 grams.
Nickel citrate ..... 20 grams.
Nickel benzoate ..... 7 grams.
Benzoic acid ..... 1.8 grams.

154. Nickel acetate ..... 20 grams.
Nickel phosphate ..... 7 grams.
Nickel citrate ..... 20 grams.
Sodium phosphate ..... 14 grams.
Sodium bisulphite ..... 7 grams.
Ammonia .....32.5 grams.

For Watt's benzoate bath see solution No. 77.

155. Placet's bisulphate, biphosphate and biacetate solutions have been given under bath No. 25.

156. Villon's solution:[16]

Nickel ammonium sulphate... 50 grams.
Nickel ammonium oxalate.... 20 grams.
Ammonium phosphate ..... 10 grams.

157. Keith's solution.[90] "For preventing and overcoming this brittleness . . . I add to a solution of nickel . . . one or more of the salts, either single or double, . . . which are formed by the union of the various organic acids, acetic, citric and tartaric, with the alkalies and alkaline earths, ammonia, soda, potassa, magnesia or alumina. . . . The result is a deposit possessing elasticity, toughness and all the hardness, brilliancy and other qualities of pure nickel. . . . These various organic acid salts may be added interchangeably and collectively, though I prefer to use, in case of the double salts of nickel, the organic acid salts which have for their bases the alkali or alkaline earth which is associated with the nickel in its double salt. . . . Of the salts which can be used to accomplish the desired effect I prefer the tartrates. . . . To twenty volumes of a solution of the double sulphate of nickel and ammonia of a gravity of 7° Bé. (sp. g. 1.0507) I add one volume of a solution of an equal gravity of neutral tartrate of ammonia in water. These solutions may for some purposes be made alkaline—for instance, in the electroplating of brass and iron, wherein local action would interpose provided the solutions were left in an acid condition."

158. An English formula:[5]

Nickel sulphate	52.5	grams.
Tartaric acid	28	grams.
Caustic potash	7	grams.

For other tartrate baths see solutions Nos. 80 and 112.

159. Classen's oxalate bath may be found under solution No. 24.

Jules Meurent[91] secures highly adherent deposits of metals or their alloys by adding to an aqueous solution of the chloride of the metal to be deposited "a compound of a metal of the alkalies containing oxygen, and adding thereto a solution of chloride of ammonia and a carbohydrate," and electrolyzing. He specifies the addition of the following: Arabit, arabinose, xylose, rharmose, or isodulcite, saccharin, isosaccharin, metasaccharin, mannite, dulcite, sorbite, triose or glycerose, tetrose or erythrose, pentose, mannose, glucose, galactose, fructose, sorbinose, formose, acrose, methylenetan, glucoazone, isoglucosamine, osone, glucosone, glucosamine, the mannoses, methylerose, mannoheptose, glucoheptose, methylheptose, manoctose, nonose, mennononose, saccharose, lactose, maltose, mycose or trehalose, melibiose, raffinose or melitose, melitriose, melectose, also the following mono-acids, the biacids and the tribasic acids: The acids arabonic, aposorbinique, trioxyglutaric, saccharonic, trioxyadipinic, desoxalic, oxycitronic, dioxypropantricarbonic, as also the aldehydes and the ketones, hexavalents—that is to say, the acids mannitic, gluconic, dextrinic, mannonic, galactonic, etc., the saccharic, mucic, isosaccharic acids, etc. "I add also all the class of gums comprising especially arabine, gum arabic, the gums of the country obtained from plum trees, cherry trees, apricot trees, etc., wood-gum, vegetable mucilage, anisie bassorin, pectic mathers. I add also the classes of collagenous and chandrogenous matters containing ossein, glutine or gelatine, and all kinds of glues, as also chondrin and chitine."

160. Meurent's nickel solution:

Nickel sulphate	50	grams.
Ammonium chloride	25	grams.
Citric acid	5	grams.
Gum arabic	50	grams.

"If the bath is too acid, it is necessary to neutralize it. Seventy-five grams of sugar or 100 grams of glucose may replace the gum arabic."

IV. Malleable Nickel.

E. Weston,[66] in his patent mentioned on page 132, claims to obtain from the solution below "A new article of manufacture—a deposit of nickel which is so tough, malleable and ductile that it can be worked in much the same way as brass or copper are worked by the operations of rolling, punching, drilling, spinning, drawing," etc.

161. Weston's solution consists of five parts of chloride of nickel and two parts of borate of nickel. The amount of water is not stated in the portion of the patent available.

162. Villon's solution of malleable nickel:[16]

Nickel ammonium sulphate .	60	grams.
Nickel ammonium oxalate..	20	grams.
Ammonium phosphate	10	grams.
Palladium oxalate	0.1	gram.

163. Kern's[92] fluoborate solution contained 8 percent metallic nickel as nickel fluoborate. In 300 hours at 1.2 amperes per square decimeter the deposit weighed 290 grams and was 5/16 inch thick. "It was bright, smooth, malleable, solid and adherent."

Two solutions previously given are claimed to yield malleable deposits: No. 23, Kugel's, and No. 139, Powell's. Deposits from the following solutions are said to be soft enough to burnish: Nos. 76, 77, 90, 106, 122, 126, 144, 147, and 149.

V. Baths Producing Thick Deposits.

Brochet,[3] Langbein,[5] Maigne and Mathey,[16] and Peters[17] all give the following:

163. Formula used in Belgium:

Nickel sulphate	50	grams.
Ammonium tartrate, neutral	36	grams.
Tannin	0.25	gram.

E. M. F. 3.5 volts; current density 0.3 ampere.

"The bath is said to yield a very white, soft and homogeneous deposit of any desired thickness, without roughness or danger of peeling off."

164. Nickel ethyl sulphate.[93] "By the use of an electrolyte which contains nickel ethyl sulphate, or the ethyl sulphates of the alkalies or alkaline earths, deposits of any desired thickness can be produced if the bath be constantly agitated by mechanical means or by the introduction of hydrogen. Agitation by blowing in air is not permissible on account of oxidation of the ethyl sulphates. Experiments with such ethyl sulphate combinations by Dr. G. Langbein & Co. resulted in formulas for prepared nickel salts, from which thick deposits of nickel capable of being polished can in a few minutes be obtained in the cold way. The salts are known in commerce as Mars, Lipsia, Germania and Neptune. In an electrolyte of given composition, which has to be kept slightly acid with acetic acid, nickeling may for weeks be carried on at the ordinary temperature without any peeling off of the deposit, and in this respect this bath surpasses all other known baths. In the course of six weeks Dr. Langbein has produced upon guttapercha matrices galvanoplastic nickel deposits 6 millimeters in thickness."—Langbein.[5]

165. A. Hollard's solution.[94]

Boric acid	65 grams.
Hydrofluoric acid (43 to 46 percent)	142 grams.
Nickel carbonate	excess.
Water	1,000 grams.

The boric acid is dissolved in 125 c.c. of boiling water, cooled, put in a rubber jar and the hydrofluoric acid added. The nickel carbonate is slowly stirred in until it remains undissolved, and then stirred for 24 hours by a motor to completely neutralize the acid. It is then filtered. At first the deposit is curly, but after three or four days of continuous operation it works satisfactorily. One may deposit nickel as thick as desired, and the deposit may be used for electrotypes on wax, guttapercha, etc. Nickel can be deposited directly on cast iron and on aluminum.

The writer can confirm Hollard's statement of the suitability of the nickel fluoborate electrolyte for thick deposits. About two years ago the writer began experiments with fluoborate solutions of several metals, obtaining deposits of considerable thickness. Last fall, as the laboratory nickel solution was not

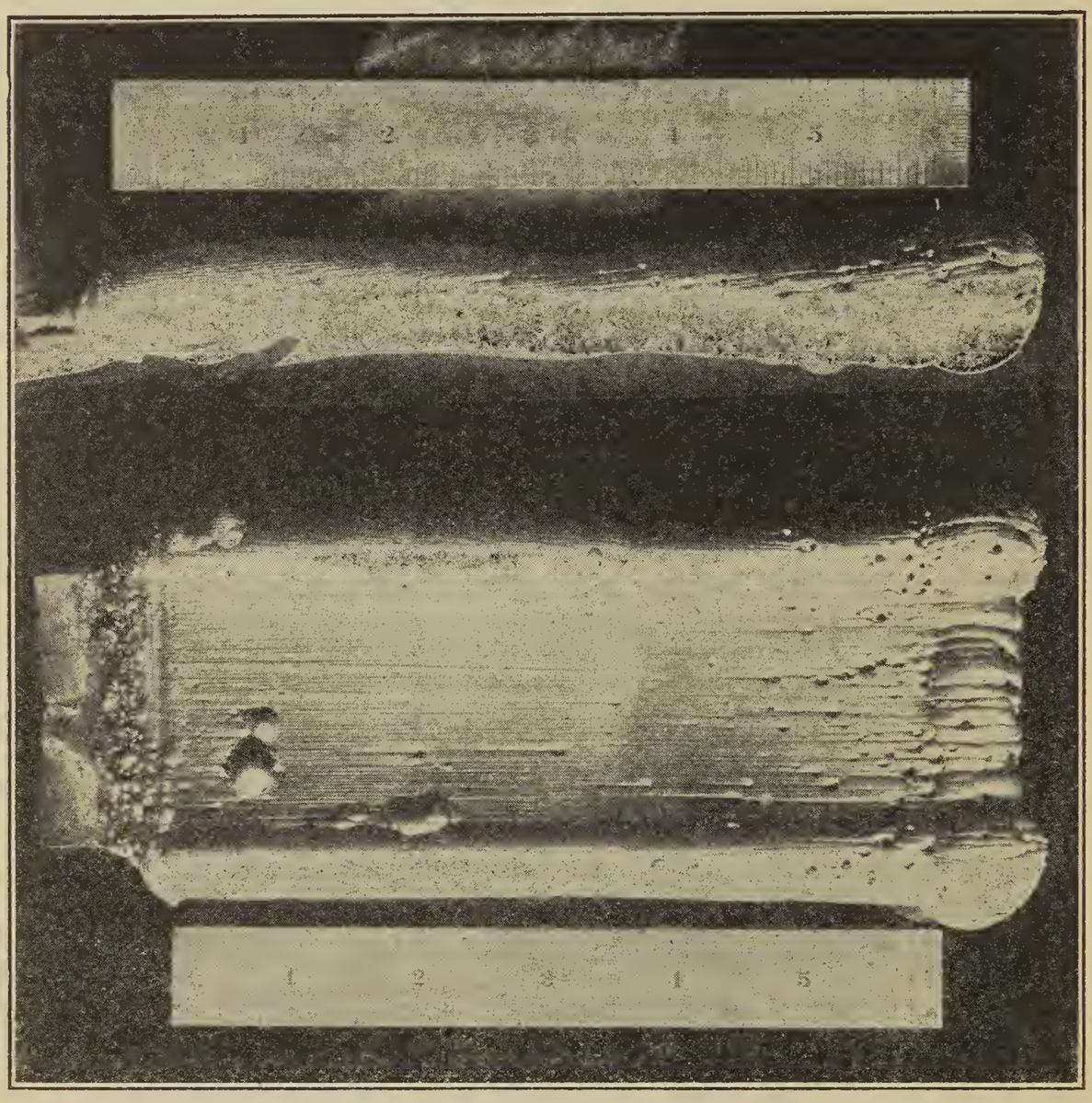

Fig. 1. Electrolytic Nickel.

working satisfactorily, about three gallons of the fluoborate solution were added to the 30-gallon nickel tank as a corrective. The solution then gave light deposits of excellent quality, but heavy deposits, run for a week or more, were badly pitted by gas bubbles which clung to the cathode. Although he has never collected and analyzed the gas, the writer is inclined to consider the trouble due to air absorbed while the solution stood idle in

the summer. After several weeks of occasional use the pitting had diminished considerably, and an attempt was made to secure a really thick deposit of nickel.

Since the regular anodes, over a foot long, were left in the tank, there was naturally an excessive deposit on the bottom of the cathode. The deposit weighs 1,500 grams, and the cathode has a maximum thickness of 30 mm. The edge is 17 to 22 mm. in thickness. The bath operated at room temperature without stirring, and no additions were made to the solution during the 85 days of deposition. The current density averaged about 0.8 ampere per square decimeter. The deposit was brilliant and very satisfactory except for the pits caused by the gas bubbles. Although the cathode was lifted from the solution every few days for examination, there was no trouble from peeling. The deposit is very hard and somewhat brittle. In comparison with those deposits of copper, iron and lead of equal thickness which have come under the observation of the writer, the smoothness and freedom from protuberances of this deposit is remarkable. It is evidently not necessary that the entire bath consist of nickel fluoborate in order to obtain thick deposits.

Of the baths previously described, No. 22, No. 91 and No. 146 are claimed to give thick deposits at ordinary temperatures.

The heating of the electrolyte to prevent curling and peeling of the deposit has already been mentioned, and doubtless the thick deposits claimed for bath No. 22 are due to the elevated temperature specified.

VI. Agents for the Production of Smooth Deposits.

"A small addition of gelatine or transparent white glue will give an exceedingly bright lustre to the nickel deposit, providing the deposit is not too heavy."—C. H. Procter.[95]

Bruce adds carbon disulphide to the nickel bath to prevent the deposit from becoming dull when it reaches a certain thickness. "This is not advisable."—Langbein[5] (p. 261).

Classen[96] obtains brilliant mirror-like electrolytic deposits of the metals by adding to the plating baths glucosides, phlorglucosides, or extract of althæa, or Panama licorice extract.

J. A. Nussbaum[97] obtains smooth, dense deposits of metals by adding to aqueous solutions of their ordinary salts small quanti-

ties of colloids, which wander toward the cathode, *e. g.*, seed mucilages (linseed), mucilage from roots or bulbs (salep), vegetable gums, albumin, glutin, chondrin, mucin, etc.

"I found that by the addition of potassium cyanide to an alkaline electrolyte of nickel the deposit of nickel formed was smoother than that obtained by using other solutions. The addition of ammonium carbonate in place of ammonia produced smoother deposits when from 1 to 2 percent of cyanide was present."—E. F. Kern.[98]

"Other conditions being the same, we shall get the smallest crystals the greater the potential difference between the metal and the solution. This is the recognized explanation for the excellent character of deposits from cyanide solution."—Bancroft.[99]

Q. Marino dissolves nickel ammonium sulphate in glycerine at 60° to 80° C. instead of in water. Foerster and Langbein[5] (p. 250) find that the deposits do not possess the good qualities claimed by the patent. "The owners of the Marino patents have apparently themselves recognized the disadvantages of the glycerine electrolyte, and have applied for a patent, according to which 15 to 20 percent of glycerine is to be added to solutions of metallic salts in water. The glycerine is claimed to act as a depolarizer, and allow of the production of lustrous nickel deposits of great homogeneity. By experiments made in this direction it was found impossible to produce a better technical effect with such an addition of glycerine than without it, in properly prepared baths."—Langbein[5] (p. 250).

VII. Nickel Electrotypes.

Of the baths mentioned, Nos. 23, 91, 146, 164 and 165 are claimed to be suitable for the production of electrotypes, etc., in nickel.

VIII. The Nickeling of Zinc.

Owing to the corrosion of zinc by many of the common nickel baths much difficulty has been experienced in plating nickel directly upon zinc. Recourse has frequently been had to a preliminary coating of copper or brass from a cyanide solution.

"Some manufacturers nickel the cleansed sheet wthout pre-

vious coppering or brassing, and claim special advantages for such direct nickeling. Sheet-zinc directly nickeled does not show the warm, full tone of sheets previously coppered or brassed. The nickel deposit upon brassed sheets shows a decidedly whiter tone than on copper sheets, and brassing would deserve the preference if this process did not require extraordinarily great care in the proper treatment of the bath, the nickel deposit readily peeling off. This peeling-off of the deposit may be prevented by avoiding too large an excess of cyanide, and by regulating the current so that no pale yellow or greenish brass is deposited." —Langbein[5] (p. 298).

The following baths are said to be suitable for the direct nickeling of zinc:

Nos. 107, 109, 138 and 139.

Electrolytic Determination of Nickel.

The methods and conditions described under Nos. 52, 53, 54, 55, 56, 57, 59, 60 and 61 for cobalt, may also be used for nickel.

No. 58, given by Classen[27] (p. 162) is stated by Perkin[28] to be less satisfactory for nickel than for cobalt, and to give rather low results.

166. Ammonium hydrate and ammonium borate.[28] Dissolve the nickel salt in 30 c.c. of water and add 70 c.c. of a solution containing 50 grams of ammonium borate dissolved in 700 c.c. of water and 300 c.c. of ammonia (sp. g. 0.88). Current 0.5 to 1 ampere at 30° C. If a slight anode deposit forms, a few cubic centimeters of strong ammonia will remove it. Time 3 to 4 hours. The method is very accurate, but the deposit is not so fine in appearance as in other methods.

There remains for consideration a few alloys of nickel with iron, zinc and other metals, but these have been purposely omitted. Although these alloys have been deposited from their various baths, they have not as yet reached any commercial importance, and it was not deemed advisable to incorporate them in this article, already bulky beyond expectation.

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THE ELECTRODEPOSITION OF LEAD

By Frank C. Mathers.

This review is divided into the following groups:

I. Lead salts of inorganic acids which are either being used or tested at the present time for commercial plating or refining.

a. Lead salts of fluorine acids.

b. Lead salts of perchloric acid.

II. Lead salts of nitrogen acids, for deposition of metallic lead.

III. Lead salts of other inorganic acids.

IV. Lead salts of acetic, oxalic and other organic acids.

V. Alkaline solutions.

VI. Solutions giving lead peroxide.

VII. Non-aqueous solutions.

VIII. Miscellaneous.

IX. Electroplating and metal coloring.

I. a. Lead Salts of the Fluorine Acids.

Leuchs (Germ. Pat. 38, 193 of 1886; Dingler, Poly. **265**, 443; thru Jahr. Ber., **39**, 2016 (1886) and Ber., **20**, 152 (1887)) first electrolyzed lead fluosilicate and lead fluoborate solutions. (Also copper, zinc and silver salts). The solution contained 300 grams of lead fluosilicate or lead fluoborate per liter. Thick, bright metallic lead was precipitated upon the cathode and firm deposits of lead peroxide upon the anode. The presence of free acid was not injurious. Carbon electrodes were used. The voltage was 1.3. Apparently the idea in these experiments, as they are described in the reviews, was to produce a storage cell or accumulator.

Betts ("Lead Refining by Electrolysis," p. 12; U. S. P. 679,824, of 1901; Eng. Pat. 1,758, of 1901; D. R. P. 134,861, of 1901) refined lead from a solution containing 4–20 percent lead and 12–25 percent SiF_6. This was the same solution used by Leuchs except that Betts employed lead anodes, since he wished to refine the lead. The lead deposit gradually assumed a "loose, rough and uneven form and crystals of lead may project from the mass sufficiently to make a short circuit." These cathodes were, from time to time, withdrawn from the solution and passed between rolls in order to produce a compact deposit, after which the cathodes were returned to the bath for further deposition. These compressed cathodes had a specific gravity of 10.28 as compared with 11.36 for pure cast-lead. Betts (U. S. P. 713,278, of 1902; U. S. P. reissue 12,117, of 1903) improved the process by the addition of a reducing agent which restrained the crystallization of the lead and gave smooth cathodes which were "characterized by substantial purity, coherence and uniformity of structure throughout, practically free from crystallization and having substantially the density and homogeneity of cast lead."

Betts (U. S. P. 713,277, of 1902; U. S. P. reissue 12,301, of 1905; Australia Pat. 1,226, of 1904; Mexico Pat. 2,261 of 1902; Canada Pat. 77,357, of 1902; Eng. Pat. 7,661, of 1902; D. R. P. 198,288; French Pat. 320,097, of 1902) has patented the use of a reducing agent with a soluble lead salt such as a lead salt of a sulpho-acid of the fatty or aromatic series or of the fluorine acids, but fluosilicate was suggested as the most suitable lead salt. A fluorine acid was defined as an acid which may be derived from an oxygen acid by the replacement of the oxygen wholly or in part by fluorine. This would of course include fluoboric, fluosilicic, fluostannic, etc. Gelatine, pyrogallol resorcinol, saligenin, ortho-amido-phenol, hydroquinone and sulphurous acid are mentioned as suitable reducing agents. Gelatine which was the most satisfactory was to be added in the proportion of 1 part by weight to 5,000 parts of the electrolyte. The deposited lead was slightly stiffer than ordinary lead and with high current densities became hard, more brittle, and of a whitish appearance and a silvery luster. The current density was from 10–20 amp. per sq. ft. (1.1–2.2 amp. per sq. dm.) and the voltage from 0.15 to 0.35.

The process has been described by Betts (Met. Chem. Eng., **1**, 407 (1903); Trans. Am. Inst. Min. Eng. for 1903; Elect. Rev., **43**, 288 (1903); Jahrb. Electrochem., **8**, 543 (1902); "Lead Refining by Electrolysis," Wiley and Sons; "Bleiraffination durch Electrolyse," Halle) and by Becker (L'Industrie electrochim., **7**, 73 (1903)). In practice the Betts process has been a success. Three refineries are in operation. Ulke (Eng. and Min. Jour., **74**, 475 (1902) and Electrochem. Ind., **1**, 105 (1903)) described the plant at Trail, B. C., Canada. Whitehead (Mines and Minerals, Jan. 1905, thru Met. Chem. Eng., **3**, 78 (1905)) said that the electrolyte (at Trail) generally contained 10 percent free fluosilicic acid and 5 percent lead, in solution as fluosilicate. Two pounds of glue to every 2,000 cu. ft. of electrolyte (0.0017 percent) was added every other day. Photographs of cathodes show rough crystalline surfaces. Other descriptions of commercial refineries are by Wolf (Western Chem. and Metall., May, 1907) and Turnbull (Mines and Minerals, Sept., 1910, thru Met. Chem. Eng., **8**, 542 (1910); Chem. Eng., **13**, 29 (1911), thru C. A., **5**, 136 (1911)). The important conditions at that time were: 12 percent SiF_6, 5–6 percent lead, 0.32 volt and 16 amp. per sq. ft. (1.8 amp. per sq. dm.). He said that 12 amp. per sq. ft. was a better density, and that in a larger plant which was under construction the lower current was to be used. The scrap in the slime amounted to 15 percent of the weight of the anodes. The anodes weighed 370 pounds (166 kilos) each, and were in the bath eight days. The anodes were placed 4½ in. (11.3 cm.) apart. Betts (Metallurgie, **6**, 233 (1909), thru C. A., **4**, 2071 (1910) and J. Soc. Chem. Ind., **28**, 530 (1909)) said the best electrolyte contained 8 percent lead, 15–16 percent SiF_6 and 0.2 to 0.3 percent hydrofluoric acid, by volume. For every ton of lead deposited 400–500 grams of gelatine was added. The temperature of the electrolyte was 30°–35° C. The loss of lead amounted to a maximum of 1½ percent of the silver present. The lead anodes were 25 mm. thick. The cathodes remained in the solution 4–5 days. Two sets of cathodes were used for one set of anodes. This means that the thickness of the finished cathodes is not over 10 or 12 mm. (0.38 in.). The article gives the cost of refining. Current yield was from 85–90 percent.

To recover the approximately one percent of lead fluosilicate which cannot be washed out of the slimes, Betts (U. S. P. 918,647, thru Met. Chem. Eng., **7**, 408 (1909)) dissolved the slime mixed with lead peroxide in hydrofluosilicic acid (15 percent) and hydrofluoric acid (5 percent). The solution, by electrolysis with carbon anodes, gave silver, copper, antimony and lead upon the cathodes in the order named and lead peroxide upon the anode. This lead peroxide was used in dissolving a fresh quantity of slime. This solution, after the deposition of the metals, is pure fluosilicic (and hydrofluoric) acid. A proper amount of it, after being changed to lead fluosilicate by treatment with lead and lead peroxide, was returned to the original electrolyte to replace that which was removed in the slime.

Betts (U. S. P. 857,378 (1907), thru Met. Chem. Eng., **5**, 327 (1907)) shunts some current from a cell when the anode is nearly consumed, to prevent the solution of the copper, etc., which is attacked when the current density at the anode and the voltage become high.

Betts (Lead Refining by Electrolysis, p. 28) says that fluoboric acid requires less hydrofluoric acid in its preparation and is a better conductor in weak solutions than hydrofluosilicic acid. However, in strong solutions, such as must be used in commercial work, the hydrofluosilicic acid has less resistance. Considering the higher cost of the boric acid, the fluosilicic acid is the more economical.

Senn (Z. Electrochem., **11**, 229 (1905)) experimented with the lead fluosilicate bath. He recommended a solution containing from 4–8 percent lead, 11 percent free fluosilicic acid and 0.1 gm. of gelatine per liter. The current density was 0.5–1 amp. per sq. dm. (4.5–9 amp. per sq. ft.). The temperature of the bath was of no importance. Lead was easily refined from its alloys with copper, bismuth and antimony. With platinum-lead alloys the slime contained a crystalline residue which showed about 60 percent lead. This was probably a compound, $PtPb_2$, which is not attacked by the fluosilicic acid ions. In neutralizing fluosilicic acid with lead carbonate, 8.19 percent of the acid was decomposed and precipitated as lead fluoride and silicon dioxide. There was a gradual decomposition of the bath during electrolysis, with the precipitation of the same insoluble products.

The current efficiency at the anode was above 100 percent (due to chemical solution of the lead) and at the cathode about 98 percent. The lead concentration of the bath dropped rapidly, due to absorption of the neutral salt by the anode slime. These things introduced serious difficulties in maintaining a uniform concentration of the bath. The lead cathodes when heated gave the odor of glue. This indicates that the glue was deposited with the metal.

Betts and Kern (Trans. Am. Electrochem. Soc., **6**, 67 (1904)) experimented with the Betts lead-fluosilicate solution as a coulometer bath. The solution which was used contained 131.5 gm. lead fluosilicate, 61.5 gm. free fluosilicic acid and 0.5 gm. gelatine per liter. The solution was first electrolyzed for four days with "refined" lead anodes at a current density of 10–12 amp. per sq. ft. (1.1–1.3 amp. per sq. dm.) to remove all impurities which might deposit with the lead. In the coulometer experiments, lead which had been thrice refined by electrolysis and which dissolved electrolytically without a residue was used as anode. The current density was varied from 8–16 amp. per sq. ft. (0.9–1.8 amp. per sq. dm.). The results agreed with those of a silver coulometer to about ±0.168 percent. Lead or platinum cathodes should be used. Copper cathodes gave low results in some cases. Results were equally good with a solution containing 85 gm. lead fluosilicate and 25 gm. fluosilicic acid per liter. A calculation of the loss at the anodes shows a current efficiency of 101.8 percent in some cases. This would rapidly change the composition of the bath. The results in this work show that the glue is not precipitated with the lead in such quantity as to make an error in the coulometer.

Jarvis and Kern (School Mines Quart., **30**, 100 (1909)) and Kern (Trans. Am. Electrochem. Soc., **15**, 441 (1909)) found that lead fluosilicate baths containing 10 gm. lead and 3.4 gm. free fluosilicic acid per 100 c.c. gave deposits which were more adherent and which were composed of shorter crystals than in the case of lead nitrate electrolytes. The current densities used were 10–30 amp. per sq. ft. (1.1–3.3 amp. per sq. dm.). Rise of temperature tended to improve the deposits. One part of gelatine, tannin or pyrogallol in 5,000 parts of the electrolyte gave a "bright, solid, coherent mass." Resorcinol was not a satis-

factory addition agent, although it restrained the crystallization somewhat. The voltage was 0.58, the current density 30 amp. per sq. ft. (3.3 amp. per sq. dm.) and the temperature 20° C. The time of runs was 185 minutes.

Richards (Met. Chem. Eng., **6**, 68 (1908)) gives a problem in metallurgical calculations dealing with the electrolytic refining of lead by the Betts process.

Anderson (U. S. P. 862,871; thru Z. angew. Chem., **21**, 1000 (1908)) has attempted to recover pure lead from the ore by electrolytically reducing galena on the cathode in a fluosilicic acid solution. This part is similar to the Salom process, whereby hydrogen sulphide is evolved and spongy metallic lead remains behind on the cathode. The current is reversed and the spongy lead which is now on the anode dissolves and is then deposited upon the cathode in a dense coherent condition.

Fischer, Thiele and Maxted (Z. anorg. Chem., **67**, 302 and 339 (1910); thru J. Soc. Chem. Ind., **29**, 952 (1910)) experimented with lead coulometers using solutions of lead fluosilicate also with the fluoborate, fluostannate, fluoantimonate, fluozirconate, fluoarsenate, fluoaluminate, and fluotitanate. The fluoborate was considered the best electrolyte. Only the fluoborate, fluosilicate and probably also the fluozirconate and fluostannate were found to be useful. The concentration of the fluoborate and fluosilicate solutions were 15 percent of lead and 15 percent of free acid in each case. The limits of current strength were 0.14–14 and 0.14–11 amp. per sq. dm. respectively. 0.1 to 1 gm. of gelatine or agar per liter prevented crystallization and did not affect the accuracy of the experiment. In all cases some free acid was present, as the neutral solutions were unstable. The electrolysis of lead fluotitanate reduced the titanium to a lower valence. Lead fluozirconate gave "beautiful white, completely adherent lead." Lead fluostannate gave good adherent deposits of lead. No reduction of the tin took place during the electrolysis. This solution could be used for coulometers. The hydrofluostannic acid, which was made by dissolving stannic sulphide in hydrofluoric acid, was so stable that hydrogen sulphide would not reprecipitate the tin. Good deposits of lead could not be obtained from the lead salts of the fluo-acids of stannous, plumbous, aluminic, ceric, arsenious, plumbic, antimonous and bis-

muthous. In most of the cases too little lead was in solution. Lead fluoarsenate and lead fluoantimonate gave good deposits, but arsenic and antimony were deposited at the same time. The lead fluosilicate solution required more gelatine than the lead fluoborate solution to restrain the crystallization. The colloid deposited with the lead. When such a deposit upon platinum was dissolved in nitric acid, a coating remained which could be rubbed off with difficulty, but which completely burned off. No such coating was obtained from deposits out of solutions which contained no colloids. In these experiments only small amounts of lead were deposited, the maximum deposition being 1.45 grams upon a surface of 72 cm. At the high current densities many crystals were formed. Addition substances were not used in most of the experiments. Increase in the amount of free acid restrained the formation of crystals. Too much free acid caused spongy deposits, and too little free acid gave basic salts or precipitates.

Mardus (Dissertation, Technische Hochschule, Charlottenburg, 1908) described experiments in refining lead from hydrofluoboric acid solutions. This paper was not available to the reviewer.

I. b. Lead Salts of Perchloric Acid.

Mathers (U. S. P. 931,944, Aug. 24, 1909; Trans. Am. Electrochem. Soc., **17**, 261 (1910); Indiana University Bulletin, **8**, 24 (1910); Chem. Ztg., 1316 (1910)) discovered the use of perchlorate baths for the electroplating and refining of lead and other metals. At a later date, Siemens and Halske (D. R. P. 223,668, Aug. 24, 1909, but first published on June 13, 1910, in Zentral-Handelsregister; French Pat. 419,769; Eng. and Min J., **91**, 902 and 1091 (1911)) patented the use of a lead perchlorate bath containing free perchloric acid and an organic colloid capable of restraining crystallization.

V. Engelhardt, of the Siemens and Halske Company (Trans. Am. Electrochem. Soc., **21**, 532 (1912)) stated that the Hagener Accumulator Works in Hagen was operating a large experimental plant which was using the perchlorate bath.

Perchloric acid is the only acid known at the present time except the "fluorine" acids, especially fluosilicic acid, which possesses the properties required for a satisfactory lead plating

or refining solution. These acids are stable under the influence of electrolytic action, and both have high electrical conductivity. Perchloric acid is the better conductor and is also more stable. The fluosilicic acid decomposes to some extent into lead fluoride and silica. Both are strong acids and are free from oxidizing action. These properties are said to prevent the formation of lead peroxide upon the anode and to produce more even solution of the anode. With proper addition agents, baths made of these acids give dense, coherent, solid deposits upon the cathode. Perchloric acid is much more stable than fluosilicic acid. It is not decomposed by boiling or by alkalies. There is a wide-spread belief that perchloric acid is explosive. Aqueous solutions of the acid are entirely stable. Perchloric acid solutions may be boiled without any loss from volatilization.

Peptone was found to be the best addition agent to restrain crystallization. Gelatine, pyrogallol, resorcine, licorice and eucalyptus extract helped to some extent, but in all these cases trees would form at the edges of the cathodes.

The Siemens and Halske Company may use a vegetable mucilage as addition substance. Their patent by Nussbaum (U. S. P. 832,024; J. Soc. Chem. Ind., **26**, 101 (1907)) claims that smooth, dense deposits of metals may be obtained electrolytically by adding to aqueous solutions of their ordinary salts small quantities of colloids which wander towards the cathode, *e. g.*, seed mucilages (linseed), mucilage from roots and bulbs (salep), vegetable gums, albumin, glutin, chondrin, mucin, etc.

The baths, as used in the laboratory experiments by Mathers, contained about 5 percent lead, 2–5 percent free perchloric acid and 0.05 percent of peptone. A current density of 2–3 amp. per sq. dm. (18–27 amp. per sq. ft.) was used. The voltage varied from 0.21–0.55 as the current density was raised from 1.6 to 4 amp. per sq. dm., with electrodes 2.2 cm. apart. The current density at the anode was double these values. The cathode deposits were solid (11.36 sp. gr.) and free from trees or rough projections. No indication of any decomposition of the electrolyte was observed at any time. The current efficiency in the laboratory experiments was above 99.5 per cent. Good deposits may be obtained from solutions containing very little free perchloric acid.

Mathers and Overman (Trans. Am. Electrochem. Soc., **21**, 313 (1912)) made a very complete study of the action of about 150 different addition agents in lead perchlorate solutions. The baths used contained about 6 percent lead and about 4 percent free perchloric acid. The following classes of substances were tried: Some inorganic substances, essential oils, resins and gums, sugars and starches, alkaloids, glucosides, proteids, and nitrogenous animal bodies, ferments and enzymes, phenols and miscellaneous. Some compounds in each class, except inorganic, showed marked beneficial action. Most compounds were without much effect. The addition substances arranged in the order of their beneficial action are: clove oil or eugenol, peptone, phloridizin, gum guaiac, licorice, phytolaccin, catechu, oil of cade, quinine, rosolic acid, starch, glycogen, pepsin, gum gambir and nitrobenzol. Photographs of excellent lead deposits obtained with the first three substances are shown. Clove oil which was recommended as the best addition substance was added to the bath regularly at a rate of ⅓ pound (166 c.c.) per ton of lead deposited. Peptone, the next best addition substance, was added to the bath at the rate of 5/6 pound (350 gm.) per ton of lead deposited. Phloridizin gave excellent deposits, but it is too expensive for use in large quantities. Rosolic acid, asafœtida, antipyrene and gum quaiac produced very peculiar, vertically striated cathodes, especially when the addition substances were added in excess. Licorice extract, succotrin aloe and aloe barbados produced very peculiar club-shaped projections from the cathodes. The deposits were solid and non-crystalline, but not smooth. No inorganic salt such as magnesium or aluminium perchlorate or nitric acid was found to be of value (Chem. Ztg., **37**, 341 (1913)).

II. Lead Salts of Nitrogen Acids for Deposition of the Metallic Lead.

Wohler (Ann. Chem. Pharm. Suppl., **2**, 135; Dingler Poly. J., **167**, 154; thru Jahr. Ber., **15**, 173 (1862)) by electrolysis of lead nitrate solution obtained crystalline leaves of lead upon the cathode. By longer passage of the current these leaves became partially but never completely copper-colored. The conditions were not known exactly, since experiments were not always

successful. He considered that the deposit was an allotropic form of lead or a lead-hydrogen compound.

Joule (Chem. Soc. J., [2] **1**, 378 (1863); thru Jahr. Ber., **16**, 280 (1863)) prepared crystalline lead amalgam by electrolysis of a lead salt with a mercury cathode. The specific gravity of the amalgam was 12.11. Analysis showed 100 parts of mercury to 194 parts of lead.

Luckow (Z. anal. Chem., **19**, 15 (1876)) found that lead separated from a neutral solution of lead nitrate partly as metal and partly as peroxide. The separation of metal was greatly increased by the presence of easily oxidizable substances by which the formation of lead peroxide was hindered.

Schucht (Z. anal. Chem., **22**, 485 (1883)) prevented the formation of lead peroxide from lead nitrate solutions by addition of organic acids, milk sugar or glycerine. Oxalic acid in excess was found to be best.

Rosel (D. R. P. 92,022, of 1896; thru Z. Electrochem., **4**, 100 (1897), and Z. angew. Chem., **10**, 308 (1897)) refined lead-silver bullion in an electrolyte of lead nitrate containing a little chloride which prevented the solution of silver. The silver remained as a slime on the anode. Nothing was said about the physical appearance of the lead deposit upon the cathode. Rosel (D. R. P. 95,194, of 1896) in a more general way proposed to use as an electrolyte such substances as would form soluble salts with lead and silver and other metals, such as zinc, which might be contained in the alloy.

Glaser (Z. Electrochem., **7**, 365 and 381 (1900-01)) has made many experiments on the deposition of lead from lead nitrate solutions. He claims that the deposition of spongy lead is caused by the simultaneous deposition of basic salts. These basic salts, which are kept in solution by the normal lead salt, will be precipitated when the solution becomes impoverished by deposition of metallic lead. This impoverishment takes place at the surface of the cathode, so the basic salts will become entangled with the deposit upon the cathode. The lead comes down in a brilliant adherent condition from solutions containing enough free acid to prevent the formation of basic salts, but too much acid will allow simultaneous deposition of hydrogen, which is injurious. A solution containing 40 gm. lead nitrate, 10 gm. sodium nitrate

and 0.63 gm. nitric acid per 100 c.c. was electrolyzed at 0.8 amp. per sq. dm. and 0.05 volt, with a lead anode and a copper cathode. There was a gradual decrease in acidity until after six hours 0.1 gm. of acid was present. This illustrates the action when acid solutions of lead nitrate are electrolyzed, *i. e.*, lead nitrate will form at the anode and hydrogen will be discharged at the cathode until the concentration of acid becomes so small that hydrogen will be no longer given off on account of over-voltage. Then the action at the anode and at the cathode will balance. The lead deposited out of this solution was homogeneous and glistening, and could be bent like a lead plate without breaking. No evolution of oxides of nitrogen could be noticed.

The above solution, after being boiled with freshly precipitated lead hydroxide, was electrolyzed at 0.4 amp. and 0.1 volt. The deposit was matted branches or trees, with white floccules near the cathode. This shows the injurious effect of basic salts in the formation of solid lead deposits. Very dilute solution of lead ions gave spongy deposits. The solution must be concentrated as regards either the lead nitrate or the sodium nitrate. Deposits from baths containing 35–40 percent lead nitrate and 10 percent sodium nitrate or 10 percent lead nitrate and 40 percent sodium nitrate, are described as being "small, dense, contiguous crystals which after several hours formed a solid homogeneous precipitate. A fringe of dense, solid crystals formed only on the borders." The deposit was not as good at 90° C. as at room temperature. It was more difficult to obtain good deposits from dilute solutions. The addition of substances like ammonium persulphate, or even hypochlorous acid, which have the power to dissolve basic salts, increases the solidity of the deposit. Additions of pyrogallol, hydrochinon, etc., also produce more solid deposits. No experiments are described in which these substances were used. Lead acetate solutions gave the same results as lead nitrate. A bath containing 100 c.c. water, 55 gm. lead acetate, 14 gm. potassium acetate, and a little acetic acid was electrolyzed with 0.4 amp. and 0.1 volt. The deposit was solid and adherent, but showed small crystals on the edges. He was unable to detect any decomposition of the acetic radicle by the electrolytic action. He claims to have obtained a lead plate 10 mm. thick, and to have plated an iron rod 30 cm. long

and 4 cm. in diameter with a uniform lead deposit 1 mm. thick. Betts ("Lead Refining by Electrolysis," p. 11) says that he has repeated all of the above experiments "as far as it is possible to follow him (Glaser), and in no case was I able to get a solid deposit of any measurable thickness." The experience of the author of this review is that the lead acetate and lead nitrate to a lesser extent give masses of crystals when the solutions are prepared according to the directions of Glaser.

Frechland (D. R. P. 140,317, of 1903; thru Jahr. Ber., **9**, 660 (1903)) prepared lead peroxide and metallic lead as a by-product by the electrolysis of 25 percent lead nitrate solution. An iron wire gauze for anode and a lead tube for cathode were used. The lead crystals which separated upon the cathode were continuously raked off to prevent short circuits. Lead oxide, hydroxide or carbonate was added continuously to neutralize the acid set free at the anode. The lead peroxide separated as a hard, thick coat 5–10 mm. thick and weighing 50–100 kg. per sq. meter. It could be removed from the anode mechanically or by heating the anode to 150–200° C., which caused the deposit to crack and fall away.

Tucker and Thomssen (Trans. Am. Electrochem. Soc., **15**, 477 (1909)) tested licorice as an addition substance in lead nitrate baths. Classen had suggested licorice in zinc plating. He claimed (U. S. P. 809,492, of 1906; French Pat. 350,964, of 1905; Eng. Pat. 12,291, of 1905; thru Z. Electrochem., **12**, 905 (1906)) that glistening deposits of metals could be obtained from baths containing glucoside or similar substances such as phloroglucosides, gummides, mannides, or extracts of plants, roots, barks, or seeds which contain such substances or derivatives, such as licorice. The solutions used contained 20 grams of lead nitrate or lead acetate and 1–5 gm. of licorice extract or root per 100 c.c. The best current density was 0.5 amp. per sq. dm. The lead deposits were unpolished but "exceedingly good, adhering firmly if the cathodes were clean and if the current densities were not too high." The effect of the addition substances rapidly disappeared and the lead deposits became poorer and poorer until after several hours they no longer adhered. The addition of more licorice would cause the bath to again give good deposits. Licorice extract gave better results

than the licorice root. The addition substances were carried over and deposited upon the cathodes, which were from 0.2 to 6 percent heavier than theory. More organic matter was deposited from baths containing licorice root than from those containing licorice extract. The greater the percent of addition substance added and the longer the bath had been used, the greater the quantity of organic matter in the cathodes. With a cathode rotating 900–2,000 times per minute, the current density could be increased 90 times over that with stationary cathodes. The deposits were greatly improved. The quantity of organic material deposited remained unchanged, but the bath deteriorated less rapidly.

Jarvis and Kern (School Mines Quart., **30**, 100 (1909)) and Kern (Trans. Am. Electrochem. Soc., **15**, 453 (1909)) tried tannin, gelatine, pyrogallol and resorcinol as addition substances in baths containing 10 gm. lead and 0.75 gm. nitric acid in 100 c.c. The addition agents, when present to the amount of 0.4 percent, restrained the crystallization to a certain extent, but the deposition was unsatisfactory except in the case of tannin. With tannin the lead deposit was more coherent and less sharply crystalline.

Sand (Z. Electrochem., **14**, 8 (1908)) showed that from a solution of lead and bismuth nitrates containing 2 c.c. of nitric acid, 15–20 gm. grape sugar and 15 gm. tartaric acid in 85–130 c.c. of solution, the bismuth precipitated first on the cathode at a constant voltage of 0.42–0.45 and with a current varying from 3–5 amp. at the start to 0.2 amp. at the end. The lead was afterwards precipitated on the cathode by raising the voltage to 0.9–0.95, with 3 amp. Rotating anodes were used. The time of each deposition was from 9 to 11 minutes.

Matuschek (Austrian Pat. 5,766, of 1909; thru Z. Electrochem., **16**, 636 (1910); D. R. P. 239,222, of 1910; thru C. A., **6**, 1887 (1912)) deposits lead from a solution of a basic double salt of nitric and nitrous acids, especially $Pb(NO_3)OH.Pb(NO_2)OH$, with the addition of lead salts, especially lead nitrate, and an excess of oak-bark tannic acid through the decomposition of which neither gallic acid nor pyrogallic acid is formed.

III. Salts of Other Inorganic Acids.

Phosphate Solutions: Phosphoric acid is stable under the action of electrolysis and is comparatively cheap, but it is worthless in lead work because lead phosphate is only slightly soluble.

Smith (Am. Chem. J., **12**, 335 (1890)) and Moore (Chem. News, **53**, 209 (1892)) said that lead could not be determined from phosphate solutions on account of the great insolubility of lead phosphate.

Brand (Z. anal. Chem., **28**, 595 (1889)) said that only metallic lead was deposited from phosphoric (or nitrous) acid solutions, but the deposited metal oxidized so readily that it could not be used for quantitative work.

Linn (J. Am. Chem. Soc., **24**, 435 (1902); Am. Chem. J., **29**, 82 (1903)) quantitatively deposited lead from phosphate solutions, prepared by precipitating lead phosphate with phosphoric acid and then dissolving the precipitate in an excess of the phosphoric acid. The lead deposit was partly crystalline and partly spongy, but sufficiently adherent to allow of thorough washing and weighing. From solutions made by adding an excess of disodium phosphate and then dissolving the precipitate in an excess of phosphoric acid, the lead was deposited as a smooth, uniform, grey coating similar to that deposited from alkaline solutions. The deposited lead contained phosphorus when a small current acted longer than required for complete precipitation or when strong currents were used. The results obtained would indicate that in a solution containing not more than 0.1 gm. of lead, and to which about 10 c.c. of sodium phosphate and 12–14 c.c. of phosphoric acid (1.71 sp. gr.) have been added, the metal can be quantitatively separated by a current of 0.0003 amp. and a voltage of 3, in 12 to 14 hours.

Gillett (J. Phys. Chem., **13**, 338 (1909)) deposited lead from a solution containing 0.13 gm. lead nitrate, 6 c.c. of 85 percent phosphoric acid and 185 c.c. of water. Decomposition voltage, or the voltage where copious deposits of lead were obtained, was 2.4 with a current of 0.5 ampere. Nothing was said about the physical appearance of the deposited lead.

Root (Jour. Phys. Chem., **1** (1903)) found a decomposition voltage of 2.85 for a solution containing 4.5 gm. sodium-hydrogen

phosphate, 15 c.c. phosphoric acid (125 gm. per liter) and 0.1 gm. lead as nitrate in 150 c.c. The decomposition voltage of 2.5 was found for a solution containing 6 c.c. phosphoric acid and 0.1 gm. lead as nitrate in 130 c.c. The deposit of lead was equally good without the sodium phosphate.

Alders and Stähler (Ber., **42**, 2685 (1909); Z. Electrochem., **16**, 832 (1910)) deposited lead as the amalgam. To the lead solution was added mercuric chloride or mercurous nitrate, 1–2 c.c. of 33 percent phosphoric acid and 1 c.c. of nitric acid in 100 c.c. of solution. A temperature of 60°–70° C., 5 amp. per sq. dm., 10–11 volts, and rotating anode, were used in the electrolysis. Lead peroxide separated at first but soon disappeared. The free acid was neutralized near the end of the electrolysis. Time of electrolysis was 20 minutes. The amalgam was washed with water, alcohol and ether, and then dried for 15 minutes in a desiccator. Arsenic acid could be used in place of the phosphoric acid, but being a weaker acid, more lead peroxide would be formed. Mercurous nitrate must be used in this case, since mercuric chloride causes the reduction of the arsenic acid to arsenious acid and finally to metallic arsenic, which precipitates with the lead.

Sulphonic Acid Solutions: Borchers (Z. angew. Chem., **4**, 596 (1891) suggested kresol-sulphonic acid in making plating solutions because of its high conductivity, easy solubility of its salts and absence of injurious by-products formed by electrolysis.

Betts (Lead Refining by Electrolysis, p. 23) found that solutions of lead salts of benzene disulphonate, phenol disulphonate and phenol sulphonate with the addition of gelatine gave excellent deposits of lead. Toluol sulphonate, naphthalene sulphonate and ethane disulphonate of lead are too insoluble to be of value. Lead methyl, ethyl or amyl sulphates with gelatine gave good deposits, but the decomposition of the salt into lead sulphate and free alcohol was so great that commercial use probably is impossible. Slight decomposition of the phenol sulphonate during electrolysis and the high cost of phenol caused Betts to cease experiments with this solution, although good deposits were obtained with it. Lead benzene sulphonate was not quite soluble enough and gave poor deposits besides. In one experiment, lead

dithionate, PbS_2O_6, solution gave an excellent deposit of lead, but later experiments failed to give satisfactory deposits. There was a continuous decomposition of the salt into lead sulphate and sulphur dioxide, the latter being reduced at the cathode so that the lead sulphide was precipitated upon the cathode. Betts thought enough of the dithionate to take out a patent for preparing the lead dithionate from manganese dithionate and lead peroxide (Eng. Pat. 15,308, of 1904).

Diament (D. R. P. 157,159) added sulphoacid and oxysulphoacid derivatives of methane as methylsulphonic, methylene sulphonic, methylene disulphonic, methylene trisulphonic and oxymethylene disulphonic acids, to baths for making lead peroxide upon lead plates for storage batteries. Perchlorates have been used for the same purpose for a long time.

Broadwell (U. S. P. 884,705 and 905,837) added to the plating bath a salt of a sulphonic acid of a carboxylic or oxycarboxylic compounds as phenols or aldehydes. He suggested naphthalene disulphonic acid. He claimed that these acids were good solvents and that metals may be deposited from their solutions without the evolution of hydrogen.

Langbein (D. R. P. 134,736, of 1902; French Pat. 320,533, of 1902; Eng. Pat. 7,995, of 1902) claims that a tough homogeneous deposit may be obtained from baths to which has been added ethylsulphuric acid or an ethylsulphate of the metal to be deposited or of some other metal or a mixture of these.

Fischer, Thiel and Maxted (Z. anorg. Chem., **67**, 302 and 339 (1910); thru J. Soc. Chem. Ind., **29**, 952 (1910)) used a solution of lead phenolsulphonate and free phenolsulphonic acid containing 85 gm. of each per liter, as a coulometer bath. The addition of 0.1–1 gm. of gelatine or agar per liter prevented crystallization of the deposited lead and did not affect the accuracy. The cathodes were washed with water and alcohol and then dried in a vacuum. The character of the deposit was improved by running at 40° C. The limits of current density were from 0.14 to 4 amp. per sq. dm.

Halogen and Other Acid Solutions: Becquerel (Borchers, "Electric Smelting and Refining," p. 462) in 1835 or 1840 treated ores to obtain lead sulphate and silver chloride, which were then

dissolved in a saturated solution of sodium chloride. Couples of zinc or iron with copper, carbon or lead precipitated the silver, copper and lead in the form of very fine particles upon the cathode.

Glaser (Z. Electrochem., **7**, 381 (1900-01)) obtained a black, spongy, non-adherent deposit by electrolysis of a solution containing 30 gm. of potassium chloride and 6 gm. lead chloride in 100 c.c. of water. 0.2 amp. and 1.7 volt were used. The high voltage which gradually increased was due to the formation of a layer of insoluble lead chloride over the anode. A better deposit was obtained from lead chloride by itself, contained in a cathode chamber made of parchment. Vigorous stirring was required. Glaser also suggested the refining of lead silver alloys by electrolysis in a lead nitrate solution saturated with lead chloride.

Elbs and Rixon (Z. Electrochem., **9**, 267 (1903)) claimed that lead was deposited from solutions containing plumbous ions in the form of large crystalline glistening leaves and from solutions containing plumbic ions in the form of spongy microcrystalline needles. The electrolysis of phosphoric acid between lead electrodes gave leafy crystals of lead on the cathode with low current densities. With higher current densities, when tests showed that plumbic ions were present, a spongy deposit was formed. Similar experiments gave spongy deposits from solutions of lead chloride, lead acetate and lead phosphite, as soon as plumbic ions were formed. The presence of microscopically-crystalline lead sponge on battery negatives was accounted for by the presence of from 0.07 to 0.14 gm. of plumbic ions per liter in the battery acids.

Elbs and Nübling (Z. Electrochem., **9**, 776 (1903)) were able to prepare plumbic salts by the electrolysis of hydrochloric, chromic and phosphoric acids, but not with hydrobromic, hydroiodic and fluosilicic acids. Plumbic sulphate had been prepared previously.

Fischer and Thiele (Z. anorg. Chem., **67**, 302 (1910)) found that lead sulphate in sodium thiosulphate and lead chloride or fluoride in sodium formate gave solutions which contained so little lead that adherent deposits could not be obtained.

IV. Lead Salts of Organic Acids.

Acetate Solutions: Keith (Eng. Min. J., **26**, 26 (1878); Borchers, p. 466; Betts, p. 10; Eng. Pat. 2,017, of 1878; thru Ber., **12**, 1027 (1879)) used an electrolyte containing 180 gm. sodium acetate per liter in which was dissolved 18.5–22.5 gm. lead sulphate. Other electrolytes which were mentioned were acidified lead nitrate or acetate, or lead sulphate in alkali chloride. The current density was 1.8–3.2 amp. per sq. ft. (0.2–0.35 amp. per sq. dm.) and the voltage was 0.4–0.5. The anodes were enclosed in muslin bags to catch the slime. The lead which was deposited in a crystalline form dropped or was raked from the cathode to the bottom of the cell. The separated lead, after the electrodes and solution had been taken from the tank, was shoveled out, washed, pressed and melted. Borchers gives these objections to the Keith process, ".....the lead is not desilverized as completely as anticipated and is always obtained in a spongy condition. This is especially the case when lead chloride solutions are used as electrolytes, whilst if acetate solutions are employed the cost of the process is increased by reason of the gradual oxidation of acetic acid and by the formation of lead peroxide at the anodes as well as by the discharge of hydrogen ions at the cathode."

Hampe (Preuss. Z., **30**, 81 (1882); thru Cent. Chem. Zentr., **13**, 519 (1882)) said that the electrolytic precipitation of lead by the Keith process was of little use technically.

Escard (Èlectricien, **34**, 387; thru C. A., **2**, 630 (1908)) gave a general history of the treatment of lead, in which he reviewed the Keith process along with those of Betts, Tommasi and Borchers.

Cowper-Coles (Electrochem. Z., **5**, 67 (1898); thru Jahr. Ber., **4**, 754 (1898)) described both the Keith and Tommasi processes.

Tommasi (Comptes rendus, **122**, 1122 and 1476 (1896); Z. Electrochem., **3**, 92 and 310 (1896-07); Eng. Min. J., **62**, 202 (1896); Borchers, p. 337; L'Industrie Electrochemique, Aug., 1903; thru Electrochem. Ind., **1**, 498 (1902-03); Z. angew. C., 244 (1898); Bull. soc. chim., **15**, 923 (1896); Eclairage Electrique **9**, parts 40, 42 and 44 (1896)) electrolyzed a solution of lead and potassium or sodium acetates with other substances

which were supposed to hinder the formation of lead peroxide upon the anode. Two semi-circular anodes 5 cm. thick and 75 cm. in radius were used in each bath; the circular cathode, 3 meters in diameter and 2 cm. thick, was made of aluminum bronze, but copper, brass or iron could be used. This cathode dipped into the bath between the anodes and was fastened to a shaft, so that it turned about 1–2 rotations per minute. Electrical connection was made by means of a brush upon the axle. Scrapers which rubbed against the rotating disc cathode removed the "small, spongy crystals" of lead. In one experiment the distance between the electrodes was given as 4 cm. The rotation of the cathode served to stir the solution and to prevent polarization. He considered one of the advantages of the electrolyte to be that the lead deposit was not so loose that it would fall to the bottom of the bath and on the other hand it was not so solid that it could not easily be scraped from the cathode. The spongy lead was mixed with charcoal and fused. Schemes of preparing litharge and white lead from it are given. The latest articles tell of using the spongy lead directly in storage battery manufacture. One small experiment, which ran for 7 hours, with a current density of 7.2 amp. per sq. dm. at the cathode, gave 100 grams of lead after fusion. This was 99.82 percent current efficiency. The loss of the anode was 1,690 gm., or 1,603 gm. after subtracting for the silver which was present. This was a current efficiency at the anode of 160 percent. Of course, there must have been other impurities in the lead besides the silver, but even then the corrosion is too great. With current densities of 1.3, 2.6 and 3.1 the voltages were 0.29, 0.58 and 0.72 respectively. Costs were given in Z. Electrochem., **3**, 341.

Cowper-Coles (Electrochem. Zeit., **5**, 67 (1898)) said that the acetic acid was oxidized during the electrolysis and that this made the electrolyte costly.

Vortmann (Ber., **22**, 2756 (1891); Chem. Ztg., 399 (1891)) determined lead quantitatively by precipitation as an amalgam. Oxalic acid, tartaric acid, ethyl alcohol and potassium iodide were of little value in restraining the formation of lead peroxide. Potassium nitrite entirely prevented the formation of the lead peroxide. The composition of the electrolyte was: 1.4 gm. of the lead salt, 1.2 gm. mercuric chloride, 3–5 gm. sodium acetate,

1 c.c. concentrated solution of potassium nitrite and enough acetic acid to re-dissolve the white precipitate which was formed. Nitric acid can be used in place of the acetic, in which case larger amounts of potassium nitrate must be used to prevent the formation of the lead peroxide. The lead amalgam was washed with water, alcohol and ether, then dried and weighed. This amalgam does not oxidize rapidly in air, so it may be weighed without difficulty.

Warwick (Chem. News, **66**, 275 (1892); Z. anorg. Chem., **1**, 307 (1892); thru Jahr. Ber., **45**, 1667 (1892)) found that the electrolysis of 0.11 gram of lead as formate with 5 to 20 cc. of free formic acid with a current of 1 to 2.8 cc. oxy-hydrogen gas per minute gave spongy lead at the cathode and more or less lead peroxide upon the anode.

Jordis (Z. Electrochem., **2**, 140 (1905)) deposited lead out of an electrolyte containing 0.1–0.2 gm. lead, 5 gm. ammonium lactate, 2 gm. lactic acid and 2 gm. ammonium sulphate in 230 c.c. Only traces of lead peroxide were formed.

Becquerel (C. R., **18**, 197 (1844)) investigated methods of metallic coloring by the deposition of lead peroxide upon objects from lead acetate solutions.

Snowden (Trans. Am. Electrochem. Soc., **9**, 223 (1906); J. Phys. Chem., **10**, 500 (1906)) electrolyzed a solution of lead acetate and acetic acid, normal with respect to both. With stationary cathodes, only small feathery crystals of lead were formed. With a current density of 0.5 amp. per sq. dm. and a cathode rotating 2,500 times per minute, "metal deposited in a crystalline and adherent form almost entirely without 'flaky' appearance which is noticeable with a stationary cathode." At higher current densities the deposit grew worse, falling off in leafy crystals. By the addition of 0.1 percent of gelatine to the solution, a matted, adherent, satisfactory deposit of lead could be obtained with the rotating cathode and a density of 1.5 amp. per sq. dm.

Brown and Nees (J. Ind. Eng. Chem., **4**, 870 (1912)) electrolyzed a solution of lead acetate and acetic acid for the preparation of spongy lead. A large anode and a small cathode were used.

Clark (U. S. P. 598,313, of 1898) produced "finely divided lead of a fibrous nature" by electrolysis of a solution of lead and

zinc acetates using a lead anode. The electrolyte was prepared by treating lead acetate with zinc until part of the lead was precipitated. At the beginning of electrolysis frothy lead was deposited, but this soon changed to the desired kind. The anode was placed in the top of the solution and the cathode in the bottom of the tank.

Marie (Congress Appl. Chem., Paris, 1900; thru Z. Electrochem., **7**, 124) precipitated the lead as sulphate or chromate, dissolved the precipitate in nitric acid with the addition of ammonium acetate, and then deposited the lead upon the cathode.

Carrier (Trans. Am. Electrochem., Soc., **5**, 230 (1904)) electrolyzed a 5 percent solution of a mixture of one part sodium sulphite and forty parts sodium acetate between lead plates. The current density at the anode and cathode was 1–2 amp. per sq. dm. The idea was to have the acetate radicle oxidized to carbon dioxide, which would then precipitate white lead. Only small amounts of a white precipitate were formed, but spongy lead was deposited upon the cathode.

Root (J. Phys. Chem., **1**, 42 (1903)) obtained good adherent cathode deposits from a solution containing 0.1 gm. lead as lead nitrate, 7.5 gm. tartaric acid and 35 c.c. aqueous ammonia in 170 c.c. Some lead peroxide was deposited. The decomposition voltage of this solution was 1.3.

Oxalate Solutions: Oxalate baths would be worthless for commercial work because of the constant decomposition of the oxalate radicle into carbon dioxide. This would not interfere with its use for quantitative work.

Classen (Ber., **14**, 1627 (1881)) said that lead could not be accurately determined by precipitation as metal, on account of rapid oxidation during washing and drying.

Classen (D. R. P. 17,864, of 1881; thru Ber., **15**, 1096 (1882)) patented the idea of depositing metals from double oxalate solutions. The ammonium double oxalate gave a grey, spongy metal, while the potassium salt gave a compact, bright deposit. The directions were: Treat the metallic salt with enough potassium oxalate to give the double salt and then add solid ammonium oxalate in excess. Sodium carbonate should then be added,

because it gives the metal a luster. It is best to electrolyze in a hot solution. Later descriptions make no mention of potassium oxalate being better than ammonium oxalate, in fact the latter salt is generally used.

Richie (Z. anal. Chem., **21**, 117 (1882)) found that from solutions of lead nitrate containing an excess of oxalic acid the lead was deposited on the negative pole as a solid adherent deposit without any peroxide being formed.

Kohn (J. Soc. Chem. Ind., **10**, 327 (1891)) qualitatively deposited metallic lead from solutions of lead nitrate containing an excess of ammonium oxalate.

Pertsch (D. R. P. 66,185, of 1892; Chem. Ztg., **17**, 285 (1893)) obtained metallic lead by the electrolysis of lead chloride dissolved in an oxalate.

Wolman (Z. Electrochem., **3**, 538 (1897)) said that it was hardly possible to determine lead by precipitation as metal out of the double oxalate solution by the Classen method on account of the difficult solubility of lead oxalate.

Root (J. Phys. Chem., **7**, 429 (1903)) found 1.55 volts to be the decomposition voltage of a double oxalate solution containing 1 gm. of lead as lead nitrate, 150 c.c. of saturated ammonium oxalate and 25 c.c. water. Nothing was said about the physical appearance of the deposited metal.

Foerster (Z. angew. Chem., **19**, 1842 (1906)) claims that the organic baths have the effects of colloids. He thinks that this is the really important thing in complex organic electrolytes. Oxalates are easily reduced to glycocolic acid (D. R. P. 204,789) and to aldehydes, which polymerize. This reduction is greater with increase in cathode potential. This would explain why some metal deposits are improved by increase in current densities. It has been known for a long time that metals deposited from complex organic electrolytes contained carbon. This is explained by saying that the organic electrolyte was changed into colloids which were precipitated with the metal.

V. Alkaline Solutions.

Becquerel (Ann. chim. phys., **8**, 403 (1843)) and Beetz (Pogg. Ann., 209 (1844)) first electrolyzed sodium hydroxide solutions of lead oxide. Becquerel said that the anode deposit was prin-

cipally hydrated lead peroxide, while Beetz said that it was hydrated lead oxide mixed with more or less lead peroxide.

Wernicke (Pogg. Ann., **139**, 143 and **141**, 111 (1870), thru Jahr. Ber., **23**, 299 (1870)) deposited lead peroxide from several solutions, such as lead acetate and tartrate in sodium hydroxide, also from neutral solutions of lead acetate and lead nitrate. Complete combination of the metallic lead with the oxygen at the anode only occurred with very low current densities. With higher current densities the precipitate contained less oxygen, and at sufficiently high current densities only oxygen was set free without any combination with the lead. The $PbO_2.H_2O$ which was formed on the anode, under the influence of secondary reactions with free acids in the electrolyte, gradually gave up its water.

Parodi and Mascazzini (Gazz. chim. Ital., **8**, 169 (1878); thru Z. anal. Chem., **18**, 587 (1879); Ber., **10**, 1098 (1877) and **11**, 1384 (1878)) obtained compact lead deposits from alkaline lead tartrate solutions containing an excess of alkali acetate. In the quantitative determination the lead was first obtained from the ore in the form of lead sulphate, which was then dissolved in sodium tartrate. Hydrochloric acid was added to this solution until a white precipitate was formed. This solution was neutralized with sodium hydroxide, then 30 c.c. of sodium hydroxide (150 gm. in 500 c.c.) was added. The volume was increased to 200 c.c. by the addition of ammonia. The deposited lead was washed and dried at 40° C. in at atmosphere of illuminating gas.

Luckow (Z. anal. Chem., **19**, 15 (1880), from Pogg. Ann., **121**, 425, Dingler, poly. J., **177**, 231, 296, and **178**, 42) said that lead precipitated in a voluminous form from alkaline solutions. In the beginning some lead peroxide was formed, but this later disappeared.

Schutzenberger (Compt. rend., **86**, 1387 (1878)), by electrolysis of a solution of sodium hydroxide with a lead anode, obtained upon the cathode a modification of lead which turned into yellow crystals of lead oxide within an hour.

Schucht (Z. anal. Chem., **22**, 487 (1883)) found that free

alkali, independent of the quantity of lead present, hindered the formation of lead peroxide. Strongly alkaline solutions gave no peroxide. The lead peroxide contained 4–5 percent of water, the amount being greater with increase of concentration of alkali. The lead peroxide also contained free alkali and nitrate which could not be washed out. The higher the current density the larger the amounts of these salts absorbed.

Smith (Am. Phil. Soc., **24**, 428 (1887)) electrolyzed a solution prepared by first treating the lead salt with an excess of disodium phosphate and then adding enough sodium hydroxide to dissolve the precipitate. The metal was washed with water, alcohol and ether, and was dried in an atmosphere of hydrogen. In all cases the metal showed a regular, compact appearance.

Brand (Z. anal. Chem., **28**, 594 (1889)) found that it was impossible to prevent the precipitation of metallic lead on the cathode during the electrolysis of alkaline solutions.

Vortmann (Ber., **24**, 2756 (1891)) quantitatively deposited lead amalgam from an alkaline bath prepared as follows: 0.3–0.6 gm. lead nitrate, 0.4–0.7 gm. mercuric chloride, 1 gm. tartaric acid, excess of sodium hydroxide, and enough potassium iodide to dissolve the brown precipitate. No lead peroxide was formed. The amalgam was washed only with water, since mercury from alkaline solutions loses when washed with alcohol. The amalgam was dried rapidly in the air. The results were generally too high, due to oxidation. Solutions alkaline with ammonia gave some peroxide. The amalgam precipitated partially as a spongy but coherent mass. More mercury was required to produce a good amalgam from alkaline solution than from acetic acid solutions.

Glaser (Z. Electrochem., **7**, 381 (1900-01)) thought that alkaline solutions would give good deposits, since potassium hydroxide or sodium hydroxide is an excellent solvent for basic lead salts, which he assumed caused spongy lead deposits. The ions in alkaline solutions are Na and PbO_2, so the lead wanders from the cathode toward the anode. This means that low voltages and vigorous stirring will be required to obtain satisfactory lead deposits. A solution prepared by saturating n./10 potassium

hydroxide with lead hydroxide by long heating was electrolyzed at 0.4 amp. and 1.22 volts. Beautiful, supple, homogeneous lead was deposited. It was possible to obtain good deposits even when hydrogen was set free simultaneously, if the solution was stirred vigorously. Lead hydroxide was present during the electrolysis. A solution of 8n. potassium hydroxide which was saturated with lead hydroxide was electrolyzed at 0.9 volt. The results were as before, except that more lead peroxide was formed and there was a greater tendency towards deposition of spongy lead. A solution prepared by shaking ammonium hydroxide with subsequent addition of ammonium acetate was electrolyzed at 0.5 volt. Solid, uniform lead was deposited. Betts (*loc. cit.*) was unable to get good deposits from solutions prepared according to the methods given by Glaser.

Elbs and Forsell (Z. Electrochem., **8**, 760 (1902)) experimented with sodium hydroxide solutions of lead. Lead anodes in sodium hydroxide solutions first remained bare and free from gas evolution. During this stage the lead dissolved as divalent ions. Grey spots came and grew, then brown spots came and gradually spread over the entire anode. Simultaneously oxygen was evolved and a yellow precipitate fell away from the anode. This precipitation gradually diminished, and finally ceased. From then on the evolution of oxygen was the only anode reaction. The phenomena do not change with increasing current density or increasing concentration of the sodium hydroxide. Reactions at the cathode were not mentioned. A solution of sodium hydroxide containing 12 gm. of lead per liter was prepared by electrolyzing normal sodium hydroxide with a lead anode. Electrolysis was continued until dark spots appeared upon the anode. Electrolysis of this solution at 0.4 amp. per sq. dm. and room temperature, with a platinum anode, gave no gas evolution, but lead peroxide was formed. With increasing current density oxygen and a yellow precipitate were formed, and, finally, at 10 amp. per sq. dm., lead peroxide, oxygen and the yellow precipitate were simultaneously formed. The yellow precipitate was lead oxide contaminated with lead hydroxide and peroxide. The physical appearance of the lead upon the cathode was not given.

Burleigh (Electrochem. Ind., **2**, 355 (1904)) recovered lead from roasted ore by dissolving the lead oxide and sulphate in hot concentrated sodium hydroxide and by electrolysis of this solution. The voltage was maintained just below 1.7, as above this zinc was deposited with the lead. Rich solutions gave large crystals of lead, which sometimes fell from the cathode to the bottom of the cell. As the solution grew weaker the lead became more spongy, until finally the lead from a very weak solution floated. Carbon anodes were used.

Jordis (Z. Electrochem., **2**, 140 (1905)) obtained lead in a spongy condition by the electrolysis of the following solution: 0.1–0.2 gm. lead, 0.7 gm. ammonium lactate, 1–2 c.c. ammonia (0.96 sp. gr.) and 2 grams of ammonium sulphate.

Brown and Nees (J. Ind. Eng. Chem., **4**, 870 (1912)) prepared spongy lead for use in making red lead, by electrolysis of a hot saturated solution of lead oxide in sodium hydroxide. Platinum anodes were used.

Bottome (U. S. P. 442,661; thru Chem. Ztg., **15**, 13 (1891)) electrolyzed anodes of silver-lead alloys in an ammoniacal bath with simultaneous passage of carbon dioxide through the solution, whereby the lead was precipitated as white lead and the silver was deposited upon the cathode.

McCutcheon (J. Am. Chem. Soc., **29**, 1446 (1907)) plated platinum wire gauzes with lead from a solution of lead sulphocyanate dissolved in potassium hydroxide.

Gardner (U. S. P. 732,843, of 1903) deposited lead for storage batteries by deposition from a solution of the oxide of the "metal" in caustic alkali. The bath was replenished by additions of oxide between charges.

VI. Lead Peroxide Deposition.

Lead most readily of all the elements forms oxide on the anode during electrolysis. Lead nitrate acidified with nitric acid is the best electrolyte for this, although other solutions may be used. The details of some of the earlier experiments have been described so briefly that little more than a reference to the work can be given here.

Becquerel (Ann. chim. phys., **43**, 380 (1830); thru Z. Electrochem., **2**, 232 (1895)) found a practical method of separating

lead and also manganese from other metals by deposition as peroxides from acetic acid solutions.

Despretz (Compt. rend., **45**, 449 (1857); Phil. Mag. [4] **15**, 78 (1858)) undertook to deposit an alloy of copper and lead by the electrolysis of molecular quantities of copper and lead acetates. He found that lead peroxide deposited upon the anode, and only traces of lead came down with the copper on the negative pole. He found that lead nitrate would give the same black deposit upon the anode, and that the presence of copper or other salts was not necessary.

Luckow (Ding. J., **177**, 296 (1865); thru Z. anal. Chem. **8**, 24 (1869)) first published a method for the quantitative deposition of lead as peroxide. The presence of tartaric acid, oxalic acid, milk sugar and similar easily oxidized organic substances, as well as salts which may be easily oxidized, *e. g.*, ferrous salts, interfered with the formation of the peroxide. The current was furnished by four zinc-copper cells. The solution contained 10 gm. nitric acid (1.2 sp. gr.?) per 100 c.c. Only small amounts of lead were present. He (Z. anal. Chem., **11**, 9 and 13 (1872), and **19**, 15 (1880)) also found that lead and copper could be determined simultaneously from a nitric acid solution. The small amounts of lead peroxide would adhere to the ordinary platinum spiral. He thought it necessary to evaporate the solution to dryness after adding a few drops of sulphuric acid, to take up the residue in a little nitric acid and to electrolyze out the last traces of lead. Determinations of larger amounts of lead were not successful, because the brown to black body separating upon the anode was not under all circumstances lead peroxide, but was a hydrate of varying lead content. If copper was present even in small amounts, less free acid was required to precipitate all of the lead as lead peroxide. From pure lead solutions 10 percent nitric acid was sufficient to cause complete deposition. The stronger the nitric acid the stronger the current that could be used without causing metallic lead to be deposited upon the cathode. Temperature was 60°–90° C.

May (Am. Jour. Sci. [3], **6**, 255 (1873)) deposited lead peroxide upon platinum foil from a solution containing 3 c.c. of strong nitric acid in 100 c.c. As much as 4 gm. of lead was deposited. The lead peroxide was removed from the foil

mechanically, transferred to a crucible and ignited to lead oxide, PbO. The platinum foil was heated, and the lead oxide which adhered to it was weighed. The calculations were made from the total weight of lead oxide. Good results were obtained. In one experiment the addition of a solution of iron and of potash caused the lead results to be 2.4 percent too low.

Herpin (Dingl. J., **215**, 440 (1875); thru Jahr. Ber., **28**, 957 (1875)) found that lead peroxide was deposited upon the positive pole during the electrolysis of 4–5 percent solutions of sulphuric acid containing small amounts of lead.

Richie (Chem. News, **36**, 96 (1877); Compt. rend., **85**, 226 (1877); thru Jahr. Ber., **30**, 1066 (1877), and **31**, 1063 (1878); Z. anal. Chem., **17**, 218 (1878)) used a platinum crucible as positive electrode and a platinum wire as negative electrode. The lead peroxide was washed with water before breaking the current, then with alcohol. It was dried at 110° C., or under a bell jar over sulphuric acid. 0.4 gm. could be precipitated in five hours, and 2 gm. over night. Many common metals, such as silver, iron, nickel, alkalies, etc., did not interfere with the separation. The solution could be either hot or cold. In a later paper (Ann. chim. phys. [5], **13**, 508 (1878); thru Z. anal. Chem., **21**, 116 (1882)) Richie used as cathode a platinum cone, shaped like the crucible, which served as anode. The distance between the electrodes was 4 mm. Alkali chromates and arsenates did not interfere with the deposition.

Schucht (Z. anal. Chem., **22**, 487 (1883)) failed to get concordant results with the method of Richie on account of the lead peroxide not being a uniform precipitate. The amount of water in the lead peroxide varied from 0.5 to 1.2 percent. The method of May, which changes the lead peroxide to lead oxide by heating, avoided this error. Schucht treated the lead peroxide in the crucible at a low heat with dry gaseous sulphur dioxide. The lead sulphate thus formed was ready for weighing as soon as it cooled. The lead peroxide could also be changed to lead sulphate by heating for 20 minutes with ammonium sulphite. The greater the amount of free acid the less was the percent of water in the lead peroxide. Lead peroxide from alkaline solutions contained more water the stronger the concentration of the alkali.

Classen and Reis (Ber., **14**, 1627 (1881)) thought that the determination of lead by precipitation as lead peroxide was unsatisfactory because the lead peroxide did not adhere more firmly to the electrodes.

Deros (Compt. rend., **97**, 1068 (1883)) determined lead in ores by first dissolving the ore and then precipitating the lead with metallic cadmium. This metallic lead was dissolved in 5–6 c.c. of nitric acid, and electrolyzed with 5 elements for 4–5 hours. The factor 0.866 was used for the lead in the lead peroxide.

Tenny (Am. Chem. Jour., **5**, 413 (1883)) changed the methods by using from 10–20 percent of nitric acid.

Weiland (Ber., **17**, 1611 (1884)) recommended a weak current in the precipitation of lead peroxide according to the method of Richie. The lead peroxide from quantities of lead greater than 0.6 gm. did not adhere well, so there was loss.

Carnelly and Walker (J. Chem. Soc., **53**, 85 (1888); thru Jahr. Ber., **41**, 459 (1888)) found that hydrated lead peroxide, $3PbO_2.H_2O$, was completely dehydrated at 230° C., and that it was stable to about 280°.

Classen and Messinger (Ber., **21**, 368 (1888)) used 30–40 c.c. of nitric acid (1.2 sp. gr.) to 120 c.c. of solution in the separation of copper and lead. The deposition was started with a current which liberated 1 c.c. of oxy-hydrogen gas per minute, and after the platinum dish showed a strong color the current was increased until 3 c.c. of oxy-hydrogen gas was liberated per minute. The deposit was washed with water without breaking the current, and then with alcohol. The dish and deposit were dried at 110° to constant weight. The deposit adhered well if not over 0.2 gm. was present. Excellent results were obtained.

Kohn (J. Soc. Chem. Ind., **10**, 327 (1891); Chem. News, **68**, 188 (1893)), for the qualitative detection of small amounts of lead, first precipitated the lead as lead peroxide from a nitric acid solution. The precipitate was then tested by ordinary qualitative means.

Rudorff (Z. angew. Chem., **5**, 198 (1892), and **6**, 453 (1893)) electrolyzed for 12 hours a solution containing 0.1 gm. lead, 2–3 c.c. nitric acid and 0.1 gm. copper in 100 c.c. of solution. The

current was furnished by three or four elements. The deposits could be washed after breaking the current, since the solution was only weakly acid. The deposit was dried at 120°. The factor 0.865 was used for the lead in the lead peroxide. In the separation of copper from lead the electrolyte contained 0.25 gm. copper, 0.012 gm. lead, 30 c.c. saturated potassium nitrate, 2 c.c. nitric acid, and water to make 120–140 c.c. A few c.c. of saturated solution of sodium acetate were added before the current was broken. This was a scheme to prevent the acid from redissolving the precipitates.

Smith and Salter (J. anal. appl. Chem., **7**, 128; thru J. Soc. Chem. Ind., **12**, 605 (1893); Jahr. Ber., **46**, 2138 (1893)) found that lead peroxide contained some bismuth peroxide when precipitated from a solution in nitric acid containing bismuth.

Medicus (Ber., **25**, 2490 (1892)) first precipitated lead as the oxalate, which was then dissolved in nitric acid. Lead peroxide was deposited from this solution according to the Classen method. Only fairly accurate results were obtained.

Smith and Moyer (J. anal. appl. Chem., **7**, 252; thru Chem. Zentr., 335 (1893)) gave the nitric acid method of separating lead from silver and mercury.

Nissenson (Z. angew. Chem., **6**, 646 (1893)) separated lead from copper in a bath containing 30 c.c. of nitric acid (1.2 sp. gr.) in 180 c.c. of solution. The current was 0.5 amp. per sq. dm. at the beginning, but was raised to 1.5–2 amp. after one hour. Six to seven hours sufficed to complete deposition. Accurate results were obtained. The lead peroxide was deposited upon a Classen dish.

Classen (Ber., **27**, 163 and 2060 (1894); Z. Electrochem., **1**, 229 and 287 (1894)) suggested the use of a platinum dish having a surface roughened with a sand blast. With such an anode 4 gm. of lead peroxide could be deposited in an adherent condition at a current density of 1.5 amp. per sq. dm. He used 20 c.c. of nitric acid (1.35 sp. gr.) in 100 c.c. of the solution, heated the bath to 50° or 60° and electrolyzed about three hours for 1.5 gm. of lead peroxide. The lead peroxide was dried at 180°–190°. For the separation of lead and copper he used 20 c.c. of nitric acid in 75 c.c. of solution, and electrolyzed the

warmed solution for about an hour at 1.1–1.2 amp. This precipitated 98–99 percent of the lead, but none of the copper. The current was broken and the solution and washings transferred to a tared platinum dish. This solution was neutralized with ammonia, then 5 c.c. of nitric acid was added, and the copper and the rest of the lead deposited at a current density of about one ampere. Voltage about 2.4. If the substance to be analyzed contained lead sulphate, ammonia was added. The lead hydroxide thus formed rapidly dissolved in the nitric acid.

Thomälsen (Chem. Ztg., **18**, 1355 (1894); Z. Electrochem., **1**, 304 (1894)) found that with small amounts of nitric acid some lead was deposited upon the cathode, especially in cold solutions. When much nitric acid was present in the solution the precipitate had to be washed without breaking the current. The addition of copper nitrate to the bath was in most cases undesirable, although it allowed the precipitate to be washed after the current was broken.

Neumann (Chem. Ztg., **20**, 381 (1896); Z. Electrochem. **2**, 231, 252 and 279 (1895-06)) used a solution containing 10 percent nitric acid. This solution was electrolyzed with 1–2 amp. at 2.3–2.7 volts, and at a temperature of 60°–70°. At higher temperatures the lead peroxide peeled off. The deposit was dried at 180°–190°. Silver peroxide was not precipitated with a weak current from a solution containing 13 c.c. of nitric acid in 180 c.c. water, or 15 percent nitric acid, if a few drops of oxalic acid were added. In the presence of less than 1 percent of arsenic in the lead material, both lead and arsenic deposit upon the cathode, but the lead afterwards dissolves and is deposited upon the anode. Simply a longer duration of the electrolysis is required. Less nitric acid increases the interference from the arsenic. The effect of selenium is similar, but weaker than that of arsenic. Manganese up to three percent has no influence if the lead nitrate solution is strongly acid and if the electrolysis is done at 70° and at a high current density, say 1.8 amp. per sq. dm.

Kreichgauer (Ber., **27**, 315 (1894); Z. anorg. Chem., **9**, 89; Jahr. Ber., 2867 (1895); Z. angew. Chem., **8**, 599 (1895)) observed that the lead peroxide precipitate had to be washed twice

with 20 c.c. portions of absolute alcohol in order to remove small amounts of nitric acid which could not be removed either by washing with water or by heating. The lead peroxide adhered best to a sand-blasted dish, which had been washed with potassium hydroxide and then with nitric acid. The adherence of the lead peroxide was best when deposited at 50°–60°. About one part of nitric acid was used to seven parts of water. The lead peroxide was dried at 120° for five minutes. Drying at a higher temperature was of no influence.

Von Giese (Z. Electrochem., **2**, 586 and 598 (1896)) found that the best conditions for lead deposition were: 12.5 percent nitric acid, 50°–55° C., 1–1.5 amp. per sq. dm., and 3–6 hours. The deposition was incomplete at 70°–75°.

Steen (Z. angew. Chem., **8**, 534 (1895)) electrolyzed a mixture of lead and bismuth in a solution containing 30 c.c. nitric acid (1.2 sp. gr.) in 200 c.c. The electrolysis was continued 15–16 hours, with three elements. The weight of the lead peroxide was too large, due to the presence of some bismuth oxide.

Smith and Meyer (Z. anorg. Chem., **4**, 267) and Heidenreich (Ber., **29**, 1585 (1896)) have separated lead from mercury in a solution containing 20–30 c.c. of nitric acid (1.3–1.4 sp. gr.) in 120 c.c. with a current density of 0.2–0.5 amp. Low acid concentration caused the lead peroxide to become detached from the anode.

Winhart (Pharm. Zentralhalle, **37**, 759 (1896); thru Z. Electrochem., **4**, 128 (1897)) tested for lead in organic substances by first decomposing the material with nitric acid and then evaporating to dryness. The residue was made acid with nitric acid and electrolyzed at 50° with 1.5–2 volts. The lead peroxide was weighed.

Wolman (Z. Electrochem., **3**, 538 (1897)) found that the solution must contain 20 percent by volume of nitric acid (1.36 sp. gr.). The precipitation was less rapid in hot solution, but adherence was better. For 0.8–1 gm. of lead, 1.5–2 amp. at 3–4 volts were used for 1½–2 hours. The lead peroxide was dried at 180°–190°, since at 100° it still contained water.

Hollard (Bull. soc. chim. [3], **19**, 911; thru Jahr. Ber., 759 (1898)) thought that the amount of lead in solution should not

be greater than 0.2 gm. The best anode was a roughened platinum cone.

Kendrick (Indiana Acad. Sci., **16**, 109 (1900)) stated that lead peroxide was formed on the anode at a voltage of 0.4.

Marie (Bull. soc. chim., [3] **23**, 563; Compt. rend., **130**, 1032 (1900)) in order to determine lead in lead sulphate or lead chromate, added ammonium nitrate to bring these insoluble salts into solution. He added 5 gm. ammonium nitrate for 0.3 gm. lead sulphate and 2 gm. for 0.5 gm. lead chromate.

Gueroult (Ann. chim. anal., **5**, 372; thru Jahr. Ber., 469 (1900)) claimed that in the presence of calcium lead could not be precipitated as the sulphate and weighed gravimetrically. He precipitated lead peroxide electrolytically from nitric acid solution by the method of Richie. The lead peroxide was then dissolved in nitric acid with the addition of sugar, or in hydrochloric acid. The lead was then precipitated as lead sulphate and weighed.

Moltkehansen (Chem. Ztg., **25**, 393 (1901); Electrochem. Ind., **1**, 351 (1903)) found that lead could be separated from 0.03 gm. manganese in a solution containing 25 c.c. nitric acid (1.42 sp. gr.) in 150 c.c. at 70° and with a current of 2 amp. for 150 sq. cm. of anode surface. The deposition was complete in 40 minutes. With 0.04 gm. manganese the current should be 2–2.5 amp. and the concentration of the nitric acid should be raised to 35 c.c., or a little oxalic acid should be used near the end of the electrolysis to redissolve the floccules of manganese dioxide. The content of lead to manganese should not be below 2 : 1.

Nissenson and Danneel (Z. Electrochem., **9**, 760 (1903)) used 1 gm. of lead substance, 30 c.c. of nitric acid (1.4 sp. gr.) in 180 c.c. of solution. This solution was electrolyzed for 1.5 hours with 1.5 amp. The lead peroxide was dried at 180°–190° for an hour.

Fischer and Boddaert (Z. Electrochem., **10**, 949 (1904)) with a cathode rotating 800 times per minute, completely deposited lead peroxide in an adherent condition in 15 minutes. 120 c.c. of solution in a Classen dish containing 20 c.c. nitric acid (1.4 sp. gr.) was electrolyzed at 95° with 10 amperes.

Hollard (Compt. rend., **136**, 229 (1903) and **138**, 142 (1904); Bull. soc. chim., [3] **31**, 239 (1904); Chem. News, **88**, 5 (1903)) found that the deposit obtained by electrolysis with platinized

platinum anodes of a solution containing 10 gm. each of lead and copper as nitrates in 300 c.c. with 12 c.c. nitric acid (1.3 sp. gr.), had very nearly the composition PbO_2, the factor being 0.861 against 0.866 for PbO_2. Electrolysis, as above, of a solution containing 0.01 gm. lead as nitrate gave a deposit having a factor 0.74. It was not known whether this variation was due to admixture of a single higher oxide or a series of peroxides. On a sand-blasted anode the factor was almost independent of concentration, being 0.853 with limits of 0.857 and 0.848. This held for baths of lead nitrate or lead sulphate dissolved in ammonium nitrate, with an excess of nitric acid in either case.

Hollard and Bertaux (Bull. soc. chim. [3], **31**, 1124 (1904); thru J. Soc. Chem. Ind., **23**, 1162 (1904)) prepared a solution for the determination of the metals alloyed with lead by depositing the lead from a nitric acid solution of the bullion. A current of 0.2 amp. was used. The last traces of lead were removed by the addition of sulphuric acid to the solution and evaporation to dryness.

Exner (J. Am. Soc., **25**, 904 (1903)) obtained adherent lead peroxide deposits upon a sand-blasted platinum dish with an anode rotating 600 times per minute. The solutions contained 0.3–1.1 gm. lead nitrate and 20 c.c. nitric acid in 120 c.c. solution. Electrolysis was with 10 amp. for 10–15 minutes. Results were excellent.

Guess (Bull. Am. Inst. Mining Eng., 1239 (1905); thru J. Soc. Chem. Ind.) deposited lead peroxide from a solution containing 10–20 c.c. nitric acid and 10–20 c.c. saturated ammonium nitrate. The current density was 1.5–2 amp. The factor for lead in the lead peroxide was 0.855.

R. O. Smith (J. Am. Chem. Soc., **27**, 1287 (1905)) used a cathode rotating 450 times per minute in precipitation of lead peroxide from a solution containing 20 c.c. nitric acid (1.4 sp. gr.), 0.3 gm. lead in 115 c.c. of solution. The temperature was 70°, voltage 4, and current density 13 amp. per 100 sq cm. A slight deposit of metallic lead was noticed upon the cathode even with 20 c.c. of nitric acid. An interruption of the electrolysis for a short time caused this lead to redissolve. The lead peroxide was dried at 230° to constant weight. Drying at too low a temperature gave too great a weight of lead. There was no further

change in weight when dried at 270°. The lead peroxide was not hygroscopic. The factor 0.8634 was determined for 0.578 gm. of lead peroxide and 0.8643 for 0.288 gm. of lead peroxide. This is the reverse of what Hollard found.

Vortmann (Ann. **351**, 238 (1907); thru C. A., **1**, 1675 (1907)) claimed that the solution must contain at least 7 percent of nitric acid to prevent the deposition of metallic lead on the cathode. All foreign metals except copper caused high results. Sulphuric, selenic and chromic acids gave high results. In these cases reprecipitation was necessary. The separation of the lead peroxide was incomplete in the presence of arsenic or phosphoric acids. In these cases the lead must be precipitated as the metal from alkaline solutions containing Rochelle salts, and then be redissolved in nitric acid and precipitated as the peroxide.

Gooch and Beyer (Am. J. Sci. [4], **25**, 249 (1908) and [4] **27**, 59 (1909)) used a special form of apparatus so arranged that the electrolyte was being constantly filtered through a platinum Gooch crucible which served as an anode. The adherence of the lead peroxide was immaterial, as the loose particles were held in a compact layer on the asbestos felt. At the end of the electrolysis the deposit was easily washed without any danger of loss. When 10 c.c. of nitric acid in 60 c.c. of solution was electrolyzed at 4 amp. per sq. dm. and 4 volts, metallic lead precipitated upon the cathode. With 3 c.c. of nitric acid there was no deposition of metallic lead. Lead peroxide in the solution slowly dissolved, so deposition was incomplete as long as detached particles floated in the solution. Addition of urea to remove oxides of nitrogen did not stop this trouble.

Westerkamp (Arch. Pharm., **245**, 132; thru Jahr. Ber., 2244 (1905)) dissolved the tin-lead alloy in red fuming nitric acid (1.52 sp. gr.) diluted with water and electrolyzed at 0.2–0.3 amp. and 2–3 volts for 12 hours.

Sand (Pr. Chem. Soc., **22**, 43 (1906) and **23**, 26 (1907); Z. Electrochem., **14**, 7 (1908); Trans. Faraday Soc., **5**, 159 and 209 (1909-10); Chem. News, **100**, 269 (1910)) precipitated lead from solutions containing 10–15 c.c. of nitric acid in 85 c.c. of solution. The time of electrolysis was 7–10 minutes with rotating anode. The solution was heated to 60° and electrolyzed with 2–3 amp. per sq. dm. In the separation of copper from

lead the hot solution containing 1 c.c. of nitric acid was electrolyzed with 2–10 amp. The higher the temperature and the lower the current density the more adherent the deposit of lead peroxide. Too much nitric acid must be avoided. Oxides of nitrogen which make the precipitation incomplete must be removed by the evaporation of the solution to dryness before electrolysis. The temperature of electrolysis must be below 97° to avoid the formation of more nitrous oxides. Large amounts of ammonium nitrate and oxides of nitrogen render the deposit loose. The addition of copper nitrate in large amounts with the use of a small amount of nitric acid, according to the method of Hollard and Bertiaux, gave results which were 0.2–0.3 percent too high. Colloids such as metallic oxides or hydroxides, *e. g.*, stannic acid, produced by hydrolysis, are precipitated with the peroxide and produce a more coherent deposit. Lead peroxide dehydrated in dry air at 200° will absorb water at that temperature in moist air. Heated at 230°, lead peroxide is dehydrated even in moist air. The factor for lead in lead peroxide dehydrated in dry air at 200° varied from 0.863 to 0.865. The electric current itself will keep the lead peroxide dehydrated if a high temperature, above 90°, and a high current density, 5 amp. per sq. dm., are used during the electrolysis. The electrode is then easily dried by dipping into alcohol and ether, and holding over a Bunsen flame. The deposit is not hygroscopic enough to absorb water during the weighing. The factor for the lead was from 0.863 to 0.865 when the lead peroxide was deposited with 5 amp. at a temperature of 90° to 97°.

British Association Committee on Electro-analysis (Electrician, **63**, 919 (1909)) reported that the discrepancies observed in deposition of lead as peroxide have shown that lead peroxide is liable to take up water, so it is recommended that the deposition should take place at 90°–95° when the deposit after drying with alcohol and ether contains only about 0.3 per cent. of water.

Benner (Min. Sci. Press, **101**, 642 (1911); thru J. Ind. Eng. Chem., **2**, 348 (1911)) electrolyzed with 4.2 amp. a hot solution containing 10 c.c. conc. nitric acid in 75 c.c., using special gauze electrodes. Temperature was 94°–97°. Under these conditions and in absence of ammonium nitrate the factor was 0.8651. He followed the Sand method.

Karr (Metal. Ind., **8**, 346 (1910); thru C. A., **4**, 2916 (1910)) considers the best method to be the deposition of the lead peroxide upon a platinum dish with ignition to PbO before weighing.

Foerster (Z. Electrochem., **16**, 832 (1910)) gives an excellent review of the difficulties in the deposition of lead peroxide.

Fairchild (J. Ind. Eng. Chem., **3**, 902 (1911)) used 30 c.c. of conc. nitric acid in 200 c.c. of solution at a temperature of 50°–60°. The process was started at a current density of 0.25 amp., which, after 1.5 hours, was raised to 0.5 amp. Ammonium acetate did not interfere. The deposit was dipped in alcohol and dried over a Bunsen burner.

Woiciechowski (Met. Chem. Eng., **10**, 108 (1912)) used a gauze electrode and followed the method in E. F. Smith's book.

List (Met. Chem. Eng., **10**, 135 (1912)) used only 2.5 percent nitric acid when only a little lead was present. With much lead, 25 percent nitric acid was said to be required to make the deposit adhere. He recommends the factor 0.855 for technical work "due to excess of oxygen in the lead peroxide."

E. F. Smith (Electro-Analysis, 1912 Ed., p. 105) recommends the use of 20 c.c. conc. nitric acid for 100 c.c. of solution and electrolysis of the hot solution, 60°–70°, with 1.5–1.7 amp. and 2.36–2.41 volts. The current should be interrupted for about five seconds when the electrolysis is half completed to allow any deposit upon the cathode to redissolve. Chlorides must be absent. In presence of other metals less nitric acid is required. The deposit should be washed without breaking the current. The dish and deposit is dried at 180°–190°. The theoretical factor 0.866 is used.

VII. Non-Aqueous Solutions.

Kahlenberg (J. Phys. Chem., **4**, 351 (1900)) electrolyzed about 4 gm. of lead nitrate dissolved in 50 c.c. of pyridine at 50° for 5 hours. The deposit was greyish and adhered well. The weight of the deposit was about 2 percent greater than theory.

Röhler (Z. Electrochem., **16**, 419 (1910)) made conductivity measurements of lead formamide dissolved in formamide solution. Lead peroxide did not form upon the anode, due to the strong reducing action of the formamide. The anode lost much more lead and the cathode gained less than theory. A saturated

solution of lead chloride in formamide containing about 4 percent of lead was electrolyzed with 0.1 amp. per sq. dm. and 0.2 volt. The cathode gained about 0.21 gm., and the anode lost 0.3, while theory gave 0.22. The deposit was "beautiful, silver grey, adherent." If the electrolyte was shaken with metallic lead and then electrolyzed in an atmosphere of hydrogen, the results agreed with Faraday's law. A solution of lead nitrate in formamide containing about 31 percent lead gave deposits more crystalline and less adherent than from lead chloride solution.

VIII. Miscellaneous.

In this list are given a number of patents, many of which do not mention lead, but which, it seems to the author, suggest valuable schemes for lead deposition.

Steenlet (U. S. P. 807,973) interposed between the electrodes a diaphragm charged with organic matter which had been treated in such a way as to be insoluble. Organic matter of any kind will probably dissolve enough to have an effect upon the metallic deposit.

Neurent (Eng. Pat. 21,149, of 1900) used the following organic substances as addition agents: Arabit, xylose, arabin, tri-oxy-adipin acid, mannit, pectins, sugars and gums. These were used in alkaline solutions.

Szirmay and Kollerich (Eng. Pat. 19,659, of 1900) used dextrine in a zinc bath.

Guess (Bull. Am. Inst. Min. Eng., 1239 (1905); thru J. Soc. Chem. Ind., **24**, 1325 (1905)) deposited copper from a solution containing a nitro compound made from a hard mineral oil which allowed a much higher current density to be employed. The addition substance was prepared from No. 4 hard oil sold by the Standard Oil Co. Di-nitro-α-naphthelene gave similar results, but required more care.

Marino (U. S. P. 607,846, of 1908) electrolyzed a bath made by adding an alkaline earth salt to a salt of the metal to be deposited so that a precipitate was formed. The solution was filtered and electrolyzed. For example, two equivalents of magnesium sulphate were mixed with one equivalent of barium chloride. After filtration a mixture of magnesium sulphate and

chloride remained. Any virtue in this must depend upon the mixed acid radicles. It seems that a simpler method of preparation could be used.

Marino (D. R. P. 104,111, of 1899; thru Jahr. Ber., 226 (1899)) used glycerine as a solvent for the metallic salts in place of water or even aqueous glycerine. If the metallic salts do not dissolve readily they should first be dissolved in alcohol, caustic alkali, or inorganic or organic acids, and then be mixed with the glycerine.

Marino (Eng. Pat. 18,350, of 1900; Eng. Pat. 22,622, of 1899; thru Z. Electrochem., **6**, 593 (1900)) precipitated the metal as carbonate, added potassium chloride, and then dissolved in an organic acid such as butyric, benzoic, formic, lactic, malic, succinic or potassium cyanide, ferrocyanide or cyanate, and in addition oxalic, boric, tartaric or citric acid with ammonium, sodium or potassium chloride. A composition might be: Solution 75, metal carbonate 15, organic acid 7, and ammonium chloride 3. Tartaric acid was said to be the best for lead.

Tunkhahn (Austria-Hungary Pat. 320,165, of 1906) used a bath containing one or more sugars.

IX. Electroplating and Coloring with Lead.

Electroplating with lead was practically impossible until the use of fluosilicate and the perchlorate bath were discovered. The directions for deposition with these solutions are given under Part I of this paper. The older books on plating say that only very thin layers of lead can be deposited. Thicker deposits could be obtained by alternate deposition and burnishing. Either dilute lead acetate solution or a bath made of five parts lead oxide and ten parts potassium hydroxide was generally used.

A fine crystalline lead powder (Pfanhauser, "Die Herstellung von Metallgegenständen," p. 46) can be deposited from a solution containing 50 gm. lead nitrate per liter with a current density of not less than 1 amp. per. sq. dm. Vigorous stirring of the electrolyte is needed.

Porous lead (Pfanhauser, p. 49) can be made by electrolysis at a current density between that needed to deposit spongy lead and massive lead. Lead nitrate solutions give stiff crystals, and

sodium or potassium hydroxide solutions of lead oxide give very delicate, tender leaflets.

Metallo-chromes are obtained by depositing very thin films of lead peroxide upon polished surfaces of nickel or iron. Exactly the right amount of deposit is required for the best display of colors. The film is fairly adherent. Becquerel's solution was made up of 14 oz. (392 gm.) potassium hydroxide, 10.5 oz. (294 gm.) lead oxide and 5 gallons (18.9 liters) of water.

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A paper presented in the Symposium on Electrodeposition of Metals, at the Twenty-Third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913, President W. Lash Miller in the Chair.

THE ELECTRODEPOSITION OF TIN

By Edward F. Kern.

This paper is a compilation of data collected from all the available literature and contributed to the Symposium on the Electrodeposition of Metals, in accordance with the request of the President of this Society.

Tin is largely used as a protective coating to articles of iron, steel, copper, brass and bronze. The process of coating large articles of iron, steel and copper by merely bringing their cleaned surfaces in contact with molten tin and then removing the excess either by means of rolls or by centrifugal machines, is so much cheaper than electrolytic methods and moreover gives such sound and perfect coatings, that the electrodeposition methods have found little application except for coating small articles and those which have an irregular surface.

A great amount of electrodeposition of tin is done for the coating of small articles such as pins, hooks, eyes, screws, clasps, etc., for which purpose this method is preferable. Another application of electrodeposition is that of giving a preliminary coating to iron or steel, which is subsequently to receive an electrodeposit of a metal which is more electropositive than iron.

The consideration of the electrolytes, as given below, was done in the following order under each of the headings: A—Acid Electrolytes, B—Neutral Electrolytes, C—Alkaline Electrolytes.

I. ELECTRODEPOSITION OF TIN BY IMMERSION.

The use of the immersion process of tinning is principally for coating small articles of copper, brass and iron, such as hooks, eyes, pins, buttons, clasps, screws, etc., with a thin, bright, adherent deposit of tin. The immersion method consists in placing the articles in contact with either metallic tin or zinc in a boiling

solution of a tin salt or a solution containing a tin salt and one or more other salts.

1. One of the most generally used immersion baths is a saturated solution of cream of tartar (potassium hydrogen tartrate) to which has been added from 15 to 30 grams of tin chloride per liter. Boil and place the articles in the boiling solution and stir with a rod of metallic tin. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Fields, "Principles of Electro-deposition," 1911 Ed., p. 212). Instead of using a rod of tin to stir the solution the articles may be placed in alternate layers with granulated or sheet tin, which will cause the articles to be coated with a white, smooth, adherent deposit of tin. (Fields, "Principles of Electro-deposition," 1911 Ed., p. 211). If the metallic tin be replaced by metallic zinc, and stannous chloride added to the solution from time to time, thicker deposits of tin on the articles may be obtained and in a shorter time. In this case no tin is being added to the solution to replace that which is deposited on the articles, so it will be necessary to reject the solution when much zinc has accumulated in it. (Fields, "Principles of Electro-deposition," 1911 Ed., p. 211; Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Metal Industry, **4**, 225 (1906)). The articles, after proper coating has been obtained, should be rinsed in water, dried by shaking with saw-dust, and polished with a scratch brush or by rolling in a polishing barrel.

2. An immersion solution which has given satisfaction for coating iron and steel articles with tin was used by Roseleur. It is prepared by dissolving 20 to 30 grams of ammonium alum and 1 to 2 grams of anhydrous tin chloride per liter of water. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Brass World, **8**, 180 (1912)). Potash alum does not give good results. Fused tin chloride is used because it does not contain any free acid, which will cause the coating to peel. The solution must be used boiling, and the iron articles must be clean of rust and grease, which are removed by an "alkali dip" and by a pickling solution. A bright coating of tin will be produced within 30 to 60 seconds. The solution must be replenished with tin from time to time by adding fused tin chloride in the original proportion to the volume of solution. As iron stands above tin in the E. M. F. series, the iron replaces an equivalent of tin in

the solution, so when iron has accumulated to an amount which causes the coating to deposit in non-adherent form the solution must be rejected.

3. The solution devised by Elsner for coating copper and brass articles, and which gives reliable results (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333) is prepared by dissolving 2 grams of sodium chloride and 2 grams of stannous chloride in one liter of water. It is used in the same manner as solution 1.

II. ELECTROLYTIC DETERMINATION OF TIN.

Tin may be quantitatively precipitated from certain solutions by electrolyzing them under such conditions of temperature, composition of solution, and current density, as have been found to give accurate results. The solutions which give the most satisfactory results are in most cases those which contain the tin either as a double salt of an organic acid or else in solution as ammonium sulpho-stannate.

1. Smith states that tin may be quantitatively deposited from a solution which contains ammonium oxalate. (Smith's "Electroanalysis," 1911 Ed., p. 169; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 149). Potassium oxalate is not advisable, as a basic salt of tin is liable to separate upon the anode. The conditions which were found to give good results are: The solution, 125 to 150 c.c. in volume, containing about 0.5 gram of tin as chloride and about 4 grams of ammonium oxalate, is acidified with 9 to 10 grams of oxalic acid (acetic acid may be used instead of oxalic acid), heated to about 65° C. and electrolyzed at C. D. of 1 to 1.5 ampere per sq. decimeter. Deposits formed under these conditions are bright and adherent.

2. Classen found that dense, bright, adherent deposits could be quantitatively formed in an acid ammonium oxalate solution. He added 120 c.c. of a saturated solution of ammonium oxalate to 25 c.c. solution containing 0.9 to 1.0 gram of stannic ammonium chloride, then electrolyzed at 30 to 35° C. with current of 0.3 to 0.6 ampere and voltage at 2.8 to 3.8. Acid ammonium oxalate must be added at intervals if a larger quantity of tin is to be deposited. Time required was about 9 hours for complete precipitation. The tin separated as a brilliant, white, adherent

deposit. It was washed, dried and weighed in usual way. (Zeitschrift für Elektrochemie, **1**, 289; **2**, 270; Smith's "Electroanalysis," 1911 Ed., p. 169; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 149).

In case the tin is to be determined in a solution containing it as potassium sulpho-stannate, Classen recommends that it be converted into the oxalate, and then electrolyze. This is accomplished by acidifying the solution with hydrochloric acid, then boiling off the hydrogen sulphide, and adding hydrogen peroxide to oxidize the tin to metastannic acid, which is a white precipitate. Add a few c.c. of sulphuric acid, neutralize with ammonia, and again add hydrogen peroxide. Filter out the metastannic acid, wash, dissolve in a solution of oxalic acid and ammonium oxalate, and electrolyze under conditions given above. Use ordinary platinum electrodes.

3. C. Engel gave the following conditions for quantitatively depositing tin by electrolysis as a bright, white, smooth, adherent deposit: Add to the solution, containing about 1 gram of tin as ammonium stannic chloride, a few c.c. of oxalic acid solution to clear the turbidity, then add 0.3 to 0.5 gram of hydroxylamine hydrochloride or sulphate, 2 grams ammonium acetate, and 2 grams tartaric acid. Dilute to 150 c.c., heat to 60 to 70° C. and electrolyze at C. D. of 0.9 to 1.0 ampere per sq. dm. and potential of 4 to 5 volts. (Zeitschrift für Elektrochemie, **2**, 417; Journal Society Chemical Industry, **15**, 219; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 151; Smith's "Electroanalysis," 1911 Ed., p. 171).

4. Campbell and Champion determined tin in ores by fusing 1.0 gram of the finely ground sample with 5 to 6 grams of a mixture of equal parts of sodium hydroxide and sulphur for 1½ hours at red heat in a porcelain crucible. The fusion was then digested with 40 to 50 c.c. of hot water, the solution filtered, and the residue washed and discarded. The filtrate was acidified with hydrochloric acid, which precipitated the tin as stannic sulphide, boiled off the hydrogen sulphide, added 10 c.c. concentrated hydrochloric acid and gradually introduced 2 to 3 grams of sodium peroxide until a clear solution was obtained. Boiled about 3 minutes, then filtered out the separated sulphur and washed. Added ammonia to the filtrate to permanent precipita-

tion, and then 50 c.c. of a 10 percent acid ammonium oxalate solution. Electrolyzed over night at C. D. of 0.1 ampere per sq. dm. and about 4 volts. Deposit of light color and very adherent. (Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 150).

In the course of any analysis, when tin is obtained as sulphide, the electrolytic determination may be conducted by getting the precipitate into solution as chloride by digesting it at boiling with 10 c.c. of concentrated hydrochloric acid and 70 c.c. of water to which is gradually added 2 to 3 grams of sodium peroxide. Then proceed in same manner as given above. (Journal Society of Chemical Industry **17**, 1073).

5. Pasztor rapidly and quantitatively deposited tin from tartaric acid solutions which contained from 4 to 6 grams of tartaric acid, 2 to 6 grams of ammonium acetate, and 1 to 1½ gram of hydroxylamine hydrochloride or sulphate per 150 c.c. volume. Electrolyzed at 60 to 80° C. at C. D. of 0.8 to 1 ampere per sq. dm., using a platinum gauze cylinder cathode, electrically coated with copper, and a rotating platinum anode at 600 r. p. m. The time required for the quantitative precipitation of 0.2 to 0.3 gram of tin was 30 to 35 minutes. The end of the precipitation was determined by H_2S test.

Pasztor replaced the tartaric acid by 4 to 6 grams of formic acid and obtained excellent results; too much formic acid injured the deposit.

Pasztor also stated that stannous sulphide dissolved in hot hydrochloric acid solution containing ammonium chloride gave a clear solution from which the tin was quantitatively deposited by the above method. (Electrochem. Zeitschrift, **16**, 281; Smith's "Electro-analysis," 1911 Ed., p. 171; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 151; Arrhenius, "Textbook of Electrochemistry," p. 274).

6. Schoch and Brown found that copper, tin, antimony and bismuth may be quantitatively deposited from a hydrochloric acid solution if suitable reducing agents (hydroxylamine hydrochloride, ammonium oxalate and oxalic acid, or formaline) are present. They claim that the reducing agent prevents the liberation of chlorine, and also causes the quantitative deposition of

these metals, which would not occur if no reducing agent were present.

They used the special form of concentric, platinum gauze, cylindrical electrodes designed by A. Fischer (Zeitsch. für Elektrochemie, **13**, 469 (1907)), and operated a small glass paddle-wheel stirrer vertically within the cylindrical anode at 800 to 1,000 r. p. m. The electrolysis was conducted with current of 1.5 amperes and at temperature between 30° and 70° C. They state that "above 75° C. the tendency of the stannic salt to hydrolize becomes so great as to render this method impracticable."

"The methods present many advantages over older methods. The electrolytes are easily prepared, because all the metals are soluble in aqua regia, and all their compounds are soluble in either this reagent or in hydrochloric acid. These electrolytes are free from odor as compared with the sulphide electrolytes frequently used for antimony and tin."

The tin was gotten into solution as chloride, diluted to 200 c.c., and the reducing agent added. The electrolysis was conducted for a period of 90 to 150 minutes, depending upon the amount of metal to be deposited.

When 4 grams of hydroxylamine hydrochloride ($NH_2OH.HCl$) was present, 0.2 to 0.4 gram of tin was quantitatively deposited within 90 to 120 minutes.

In the cases when 5 to 10 grams of ammonium oxalate and 10 to 20 grams of oxalic acid were added, and the electrolysis conducted at temperature varying from 30° to 70° C., the complete deposition of 0.2 to 0.3 gram of tin was accomplished in 90 minutes, and 0.7 gram of tin in about 150 minutes.

When formaline was present, the deposition of tin was incomplete, but was more complete than when no reducing agent was added (Trans. American Electrochem. Soc., **22**, 268 (1912)).

7. Classen discovered that a dilute solution of tin containing an excess of ammonium sulphide would yield a quantitative deposit of the metal, but that the deposits formed in a sodium or potassium sulphide solution were dark gray and non-adherent. (Smith's "Electro-analysis," 1911 Ed., p. 170; Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 150). The conditions for obtaining a satisfactory deposit of tin from ammonium sulphide solution containing the tin as ammonium

sulpho-stannate are: 150 c.c. solution containing an excess of ammonium sulphide, heated at 50 to 60° C., and electrolyzed at C. D. of 1 to 1½ ampere per sq. dm. and potential of 4 to 5 volts. (Arrhenius, "Textbook of Electrochemistry," p. 274).

Use of Rotating Electrodes.

The use of rotating anodes, revolved at 300 to 500 times per minute, enables the quantitative precipitation of tin to be made from ammonium oxalate solutions and ammonium sulphide solutions in 20 to 30 minutes, giving a deposit like polished silver. The electrolysis is conducted with C. D. of 5 to 8 amperes per sq. dm. and E. M. F. of 5 to 8 volts. (Smith's "Electro-analysis," 1911 Ed., p. 172).

Removal of Tin Deposits from the Cathode.

The deposit of tin on the platinum cathode may be readily removed by fusing with potassium bisulphate, or dissolving in a mixture of nitric acid and oxalic acid, or by means of dilute hydrochloric acid with a piece of metallic zinc in contact with the cathode. (Smith's "Electro-analysis," 1911 Ed., p. 169).

III. ELECTRODEPOSITION OF TIN BY SEPARATE CURRENT.

On account of the whiteness of tin and it not becoming tarnished by exposure to the atmosphere, an electrolytic deposit of this metal is much desired. There are many uses which could be made of small metallic articles which are coated with an adherent, smooth, dense, bright deposit of tin, but the difficulty of obtaining such a deposit has hindered the larger practice of electroplating with tin.

A number of electrolytes have been suggested, some of which have been patented, but the choice of the proper solution for the coating of articles of iron, steel, copper, brass or bronze will in most cases largely depend upon the character of the work to be done, and the available conditions, such as the source and quantity of current, means of controlling the temperature of the electrolyte, size of the articles, and the method of handling and treating them before and after the electrolysis has been conducted.

The electrolytes which are given below are those which have been recommended and used for electroplating of tin. In many

cases the published composition of the electrolytes was given in either ounces or pounds of the ingredients per gallon, but in order to allow ease of comparison of the different solutions, their compositions were calculated into grams per liter, and temperatures were changed from Fahrenheit into Centigrade. One ounce per gallon is equivalent to 7.5 grams per liter.

1. Good deposits of tin may be produced by using an electrolyte containing stannous chloride and acid ammonium oxalate. One liter of this solution is prepared by dissolving 25 to 30 grams of crystallized stannous chloride in about 400 c.c. of water, 55 to 65 grams of ammonium oxalate and 3 to 4 grams of oxalic acid in about 400 c.c. of water. Add the oxalate solution to the tin solution with vigorous stirring, so that the white precipitate which forms at first will dissolve. Dilute to 1 liter and boil a few minutes. The deposits formed from this electrolyte are said to be excellent, and further, the anodes corrode normally, so there is no need of adding tin salt to the electrolyte from time to time. This solution has the advantage that it can be mixed with a similarly prepared copper solution, and the mixed solution used for depositing a coating of bronze. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331. Field's "Principles of Electro-deposition," 1911 Ed., p. 213).

2. Roseleur's tin bath is recommended as giving the most satisfactory deposits of any of the generally-used electrolytes. It is prepared by dissolving 10 to 12.5 grams of sodium pyrophosphate in 1 liter of water and suspending 1 to 1.5 gram of fused stannous chloride in the solution by placing it in a copper screen or in a linen bag. Agitate till all the tin chloride is dissolved. The solution is at first cloudy, but finally becomes clear and is ready for use. Voltage required from 1.5 to 4 volts. Use pure tin anodes.

It is stated that any metal may be coated with tin in this solution, the deposit having a dead-white lustre resembling silver, which may be polished by either scratch-brushing or by burnishing. Articles of zinc, copper, brass and bronze may be directly tinned in this bath, but those of iron and steel must be first tinned in an immersion solution (See I, 2) or else electro-coppered then scratch-brushed and finally placed in the tin bath. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248;

Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331; Watt and Phillip, "Electroplating and Electrorefining," 1911 Ed., p. 344; Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 439).

The Roseleur electrolyte is the one most generally used for electro-tinning. It is capable of giving the whitest deposit of any of the tinning baths which are in general use. The objections to it are that it must be worked hot, that heavy deposits cannot be obtained except after a period of several hours, and that the anodes do not dissolve normally, which necessitates that a concentrated solution of tin chloride be added to the working solution from time to time.

The Roseleur bath has been modified in concentration by other electroplaters: Weiss used a solution containing 1 gram of fused stannous chloride and 5 grams of sodium pyrophosphate per liter. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249). A solution recommended as giving excellent results is prepared by dissolving 15 grams of sodium phosphate crystals in 1 liter of water, and adding 7.5 grams tin chloride. Work at low current density. (Metal Industry, **4**, 138 (1906)). Another solution, said to have been recommended by eminent authorities, contains 37 grams sodium phosphate crystals and 20 grams fused tin chloride per liter. The tension required for this electrolyte was given as 1 to 1.5 volt, when worked hot. (Metal Industry, **5**, 376 (1907)).

3. An electrolyte which gives good results when electrolyzed at ordinary temperature is prepared by dissolving 15 grams of ammonium chloride and 30 grams of fused stannous chloride in a liter of water. Use pure tin anodes, and regulate the current so as to avoid pulverulent deposits. (Metal Industry, **9**, 519 (1911)).

4. An electrolyte which is strongly recommended as giving excellent results is prepared by dissolving 45 grams of diammonium stannic chloride (pink salt) per liter of water. Electrolyze at tension of about 1.5 volt. (Metal Industry, **5**, 376 (1907); Zeitschrift für Elektrochemie, **7**, 34).

5. A good, lustrous deposit of tin may be produced by using an electrolyte prepared by dissolving 30 to 60 grams of cream of tartar (potassium hydrogen tartrate) in a liter of water, and

adding 7.5 to 15 grams of tin chloride crystals. Use pure tin anodes, and electrolyze at temperature not less than 70° C. at E. M. F. of 3 to 5 volts. A good lustrous deposit can be obtained in 20 to 30 minutes; scratch-brush with a soft steel brush, or polish on a soft buff-wheel using Vienna lime and kerosene. Keep the solution between 5 and 6° B. (Metal Industry, **6**, 162, 227 (1908); **7**, 227 (1909)).

6. A solution which has been used considerably for tinning articles of iron, steel and brass is prepared by dissolving 60 grams of caustic soda in about 800 c.c. of water, and 22.5 grams of fused stannous chloride in small amount of water, then pour the tin solution into the caustic solution and dilute to 1 liter. Electrolyze cold, using pure tin anodes, and potential of 1 to 1.5 volt. (Bedell's "Practical Electroplating," 1909 Ed., p. 143). If the solution becomes impoverished in tin it should be revived by adding fused stannous chloride. If solution assumes a milky appearance, add caustic soda until it clears. Keep at about 11° B.

While the work is being plated it takes on a frosty appearance which is usually porous; the work should then be removed from the bath and scratch-brushed. This may have to be repeated several times, if thick deposits are desired. When mechanical plating-barrels are used scratch-brushing will not be necessary, as the rolling and the rubbing of the articles cause them to become burnished. Articles of iron and steel must first be given a slight coating of copper in a copper cyanide electrolyte, preferably hot.

7. A tin bath which has given satisfaction is prepared by dissolving 12 grams of metallic tin in hydrochloric acid, evaporating to expel the free acid, then adding to a solution of 25 grams of potassium hydroxide, and diluting to 1 liter. The addition of stannous chloride must be made from time to time as needed. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 330).

8. Elsner used an alkaline electrolyte which he recommends as having given satisfaction for electro-tinning iron and steel. It was prepared by adding 25 grams of tin tetrachloride to 1,000 c.c. of water and adding sufficient caustic potash to give a clear solution. He used cast tin anodes, and required a potential of 3

to 5 volts. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248).

9. Hearn prepared an electrolyte which he used for general work by dissolving 21 grams of tartaric acid and 30 grams of caustic soda in 1 liter of water, then adding 3 grams of fused tin bichloride. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249).

10. Fearn recommends a bath which he prepared by dissolving 25 grams of tartaric acid in about 400 c.c. water, 75 grams of caustic potash in about 400 c.c. water, and 1.3 gram of fused stannous chloride in 50 c.c. water. The caustic solution was added to the tin solution, then the tartaric acid solution mixed with it. Diluted to 1 liter, and electrolyzed cold or hot. Thick bright deposit. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249).

11. Steele prepared an electro-tinning solution by dissolving 5.5 grams of caustic potash, 16.5 grams of potassium carbonate, and 66 grams of sodium carbonate in 1 liter of water, after which he added 17.5 grams of tin dioxide, 1 gram potassium cyanide and 1 gram zinc acetate. Filtered before using. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249; Watt and Phillip, "Electroplating and Electrorefining of Metals," 1911 Ed., p. 345).

12. An alkaline bath proposed by Elsner for tinning iron and steel articles is prepared by putting 11 grams of tin bichloride in 1 liter of water, then adding a solution of potash lye of 10° B. until the precipitate is dissolved, and 10 grams of potassium cyanide. (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 440).

13. Good deposits of tin may be produced by dissolving 1.5 grams of fused stannous chloride, 80 grams of potassium carbonate, and 1 gram of potassium cyanide, separately in water; then adding the cyanide solution to the tin solution and finally stirring in the carbonate solution. Dilute to 1 liter. This solution is not a very good conductor of current, thus requiring a high voltage; still satisfactory deposits may be obtained. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 331).

14. Salzedes used a bath for tinning iron which he prepared by adding 10 grams of potassium cyanide, 110 grams of potassium carbonate, and 2.5 grams of stannous chloride to 1 liter of water.

By electrolyzing with voltage at 4 to 5, a heavy dense deposit was rapidly obtained. (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 441).

15. An electrolyte patented by Fearn in 1873 contained 1.2 grams of fused tin bichloride, 111 grams caustic potash, 111 grams potassium cyanide, and 111 grams of sodium pyrophosphate per liter. Each of these chemicals was separately dissolved in water; the tin solution was poured into the potash solution with constant stirring, then the cyanide solution was added, and finally the pyrophosphate solution. Electrolyzed at ordinary temperature. Bright thick deposits were obtained. It was found necessary to add fused tin chloride to the bath from time to time, as the anodes were not dissolved as rapidly as the tin deposited. (Watt and Phillip, "Electroplating and Electrorefining of Metals," 1911 Ed., p. 345; McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 248).

16. The following solutions are capable of giving good white deposits upon all metals, and may be used cold:

(a) Solution for electro-tinning brass, bronze and copper; 7.5 grams of caustic potash, 7.5 grams of stannous chloride, and 35 grams of potassium cyanide per liter.

(b) Solution for steel, wrought iron and cast iron; 15 grams of caustic potash, 15 grams of stannous chloride, and 35 grams of potassium cyanide per liter. Dissolve the caustic potash in water, add the tin chloride, then the potassium cyanide. If the tin chloride contains any iron, a precipitate will remain suspended in the solution, which should be filtered off. These solutions may be used either cold or hot. Better deposits are formed in the warm solutions. Use as large anode surface as possible and electrolyze at tension of 2.5 to 3 volts. (Brass World, **7**, 121 (1911)).

A more concentrated caustic solution than the above is said to have given very satisfactory deposits. It contained 60 grams of soda lye, 45 grams of fused stannous chloride, and 12 grams of potassium cyanide per liter. Electrolyzed at 1.5 volt. (Metal Industry, **5**, 376 (1907)).

17. J. C. Beneker obtained U. S. Patent 921,943, assigned to the Meaker Company of Chicago, for a tin electrolyte, the composition of which is 125 grams of sodium hydroxide, 75 grams

of sodium thiosulphate, and 50 grams of crystallized stannous chloride per liter. The solution is prepared by dissolving each of the salts separately, mixing the stannous chloride solution with the hydroxide solution, then adding the thiosulphate solution. It is stated that possibly the chief constituent of the prepared solution is sodium thio-stannate (Na_2SnS). By using pure tin anodes, the deposit is produced without the formation of sponge or tree-like crystals, even when operated at high current density. The electrolyte may be used either cold or hot, but preferably hot. (Electrochemical and Metallurgical Industry, **8**, 285 (1909)).

18. An electrolyte of composition similar to the Beneker solution contains 120 grams of sodium hydroxide, 60 grams of sodium hyposulphite, and 30 grams of chloride of tin per liter. (Metal Industry, **9**, 90 (1911)).

19. An electrolyte which is recommended to give excellent deposits of tin is prepared to contain 90 grams of caustic soda, 15 grams of sodium hyposulphite, 15 grams of sodium chloride and 30 grams of tin chloride crystals per liter. This solution may be used either cold or hot, but gives better results when hot. Use anodes of pure tin. Metal Industry, **8**, 87 (1910)).

Conditions Necessary to Obtain Bright, Dense, Adherent Deposits of Tin.

The articles to be electroplated in any of these solutions must be carefully cleaned in a strong potash solution, then rubbed with lime and subsequently thoroughly washed in clean water before placing them in the electrolyte. No time should be lost in getting the articles immersed in the plating solution directly after washing. (McMillian-Cooper, "Electrometallurgy," 1910 Ed., p. 249).

There is one drawback in depositing tin from most of the baths which are in general use, namely, the anodes are not dissolved in the same ratio as tin is deposited on the cathode, consequently the strength of the bath must be kept up by the addition of a tin salt. This is best accomplished by allowing a concentrated solution of the tin salt to drip constantly into the bath during the time it is working. (Watt and Philipp, "Electroplating and Electrorefining," 1911 Ed., p. 342).

Tin baths should not be used at temperatures below 20° C.; as a general rule, the higher the temperature the better the deposit.

Too high current density causes a spongy deposit, which does not adhere; whereas, with a suitable current density, a dense, reguline deposit will be obtained. (Langbein-Brannt, "Electrodeposition of Metals," 1909 Ed., p. 441).

W. Pfanhauser conducted a number of experiments on the formation of spongy and crystalline deposits of tin by electrolysis. He stated that the electroprecipitation of tin as thick adherent deposits is possible only in very concentrated tin-salt electrolytes, and those which contain no cations which will give rise to strongly dissociated solutions about the cathode. The best conditions for good tin deposits were found to be circulation of electrolyte, low current density, and high concentration of tin in the electrolyte. Spongy deposition is caused by poor circulation, dilute solutions, high current density, acid solutions, and impure solutions. Crystalline deposits form when the electrolyte contains no cations which are capable of forming alkali hydroxides or similar compounds, which are accompanied by the liberation of hydrogen. He used Roseleur's solution of tin chloride and sodium phosphate (See III, 2), and concentrated solutions of tin tetrachloride and stannous chloride. (Zeitschrift für Elektrochemie, **8**, 41 (1902); Electrochemist and Metallurgist, **2**, 42 (1902); Journal of Society of Chemical Industry, **21**, 261 (1902)).

In an article on "The Electrolytic Preparation of Tin Paste," the statement was made that "A spongy deposit may be due to various causes, but may be obtained nearly always by using too high a current density at the cathode. This results in an impoverishment of the electrolyte near the cathode with respect to the ions of the metal to be deposited, so that some other metal, and also generally hydrogen, is simultaneously deposited. It is under such conditions that the metal deposit becomes spongy." (Electrochemical and Metallurgical Industry, **3**, 59 (1905)).

IV. ELECTROLYTIC RECOVERY OF TIN FROM TIN-PLATE SCRAP, AND ELECTROLYTIC TREATMENT OF TIN ORES.

The manufacture of tin-plate, which contains from 2 to 4 percent of tin, consumes the major portion of the world's supply of tin. The recovery of tin from tin-plate scrap and old tin cans therefore presents a very encouraging metallurgical proposition.

A number of processes have been developed and a number patented, but on account of the cost of obtaining sufficiently large quantities and a constant supply of the scrap at any one center, the recovery of tin and iron from tin-plate scrap has resulted in the majority of cases in economic failure.

The recovery of tin from tin-plate scrap is accomplished by either mechanical, chemical or electrochemical means. An example of mechanical recovery is the heating of the scrap with sand in revolving cylinders, which recovers only a portion of the tin. The chemical recovery is accomplished by dissolving the tin from the scrap by means of solutions of acids, alkalies or oxidizing salts, or else exposing it to an atmosphere of dry chlorine.

The most successful method of detinning is that which was developed by Goldschmidt at Essen, which consists in treating the dry tin scrap with dry chlorine in carefully cooled iron cylinders (Electrochemical and Metallurgical Industry, **7**, 53 (1909)). The tin-plate scrap is prepared for treatment by removing adhering grease with a hot caustic solution and by washing, after which it is heated in furnaces in order to remove organic matter and, in case of old tin cans, to recover the solder. (The melting point of solder is between 240° and 225° C. Solder contains from 35 to 40 percent of tin and 65 to 60 percent of lead.) The cleaned and dry tin scrap is then pressed into bundles, placed in large gas-tight iron cylinders, and dry chlorine forced in under a pressure of several atmospheres, keeping the cylinders cool. As soon as the pressure remains constant, the detinning has been completed, the tin having been converted into liquid stannic chloride. This salt, together with the excess of chlorine, is removed, and the bundles of iron scrap are washed and are ready to be charged into the open-hearth furnace for the production of steel, or else melted in a cupola and cast into any desired shapes of cast iron.

The electrolytic methods which have been proposed for the recovery of tin from scrap and for the treatment of tin ores are many; in the majority of cases for the treatment of tin scrap the material is made an anode in some suitable electrolyte. The electrolytes which have been proposed are the following: Dilute hydrochloric acid; dilute sulphuric acid; mixed solutions of

hydrochloric, sulphuric and nitric acids; acidified solutions of sulphates or chlorides; solutions of a ferric salt; solutions of a stannic or stannous salt, either acid, neutral or alkaline; caustic solutions; or caustic solutions containing one or more salts. In cases when either acid or neutral electrolytes are used the tin scrap is made the anode by being placed in a wooden or in a solution-proof container, and when the electrolyte is alkaline the anode container and the cell are made of iron. The cathodes are sheets of either copper, iron or tin-plate. The electrolysis is conducted with a difference of potential between the anodes and cathodes of from 1 to 3.5 volts. The tin is deposited on the cathode as non-adherent crystals or as sponge, which is collected, washed, melted and cast into bars. The tin which is recovered by electrolytic stripping contains more or less iron and lead, so that in case pure tin is wanted the bars must be refined.

Electrolytic Recovery of Tin from Tin-Plate Scrap.

1. Smith electrolytically recovered tin from tin-plate scrap by using an electrolyte of dilute sulphuric acid (1 part of acid of sp. gr. 1.7, and 9 parts of water). The scrap was placed in wooden baskets, which were the anodes, and the tin deposited on sheet copper cathodes. The tin at the start formed as sponge, but finally changed to extremely fine crystals of pure tin, which fell to the bottom of the cell (Journal Soc. Chem. Ind., **4**, 312 (1885)).

Englehardt's electrolytic detinning process is the use of a 14° B. sulphuric acid electrolyte (15 grams of conc. acid per 100 c.c.), the tin scrap being placed in a non-conducting basket, and the metal deposited on a sheet metal cathode. He obtained an electrical efficiency of about 60 percent (Zeitsch. für Elektrochemie, **7**, 34 (1912)).

2. German patent 12,883 and English patent 8,988 were granted to Gutenson and Fenwick for the use of an acid sulphate electrolyte, which contains chlorides, for the recovery of tin from tin scrap and other tin-containing materials (Schnabel-Louis "Handbook of Metallurgy," II, 1907 Ed., p. 546).

3. Nauhardt used an electrolyte containing 10 percent of sulphuric acid and a small quantity of ammonium sulphate for the recovery of tin. The electrolysis was conducted at a current

density of 2 to 3 amperes per square foot, and E. M. F. of about 1.7 volt. The deposit formed as fine crystals. When the tin begins to deposit as sponge, an addition of ammonium sulphate is made (Jour. Soc. Chem. Ind., **21**, 261; Chem. Zeitsch., **26**, 50 (1902); Electrochemist and Metallurgist, December, 1901). German patent 118,358 and English patent 21,942 were issued to Nauhardt for the use of an acid ammonium sulphate electrolyte for detinning.

4. Changy used an electrolyte of stannous chloride to which ammonium chloride or hydrochloric acid was added, making the scrap the anode by placing in a wooden basket (Schnabel-Louis, "Handbook of Metallurgy," II, 1907 Ed., p. 546).

5. Tommasi proposed to collect the tin sponge, produced by electrolytically detinning in an hydrochloric acid solution of stannous chloride, by using a bronze cylinder cathode from which the sponge would be removed by scrapers as the cylinder was revolved (Elektrochemische Zeitschrift, **13**, 34 (1906)).

6. Gelstharpe built a commercial experimental plant for detinning at Manchester, England. The electrolyte contained about 1.25 percent of hydrochloric acid by weight and a small quantity of sulphuric acid, the latter being added in order to prevent lead dissolving in case the scrap or old tin cans contained any solder. The scrap was placed in wooden crates and suspended between tin-plate cathodes in a shallow tank. It required about half an hour to remove the tin from the scrap, it being deposited as sponge. The sponge was collected, washed, pressed into blocks, dried, melted and cast into bars. The electrolysis was conducted at current density of 15 amperes per square foot, and potential of 1 to 2 volts. It was found necessary to add a small amount of hydrochloric acid at intervals so as to keep up the acidity of the electrolyte (Electrochemist and Metallurgist, **1**, 276 (1901)).

Gelstharpe states that "when the tin is required in the form of bright fern-leaf or needle crystals, both of which are eminently suitable for the manufacture of tin compounds, the washed tin sponge is placed in a flannel bag which forms the anode in an electrolyte composed of a 5 percent acid solution of stannous chloride, free of arsenic. The tin is deposited as beautiful bright leaves of tin on the cathodes which are tinned sheet iron" (Electrochemist and Metallurgist, **1**, 278 (1901)). By operating at

a current density of 25 amperes per square foot the current efficiency averaged 50 percent, being low on account of the hydrogen which was simultaneously deposited with the tin (Trans. Faraday Society, **1**, 113 (1905)).

Gelstharpe and Gelstharpe secured English patent 2,282 for mechanical appliances in connection with the cell used for recovering tin from waste tin cuttings (Electrochemist and Metallurgist, **1**, 130 (1909); Mineral Industry, **11**, 235).

7. Quintaine received United States patent 699,012, reissue 12,214, and German patent 118,358 for the use of a dilute sulphuric acid solution containing tin nitrate and an ammonium salt, preferably ammonium sulphate. The solution is prepared by dissolving the tin nitrate, then adding the ammonium salt and tin chloride until the solution becomes clear. The tin scrap is made anode by being placed in a wooden crate or in a copper wire basket and using a sheet lead cathode. The electrolysis conducted at 20 to 25 amperes per square meter (1.9 to 2.3 amperes per square foot), and tension under 1.7 volt. The deposit of tin separates as a sponge so long as the electrolyte is acid, but as the bath becomes neutral the deposit becomes more pulverulent and crystalline (Electrochemical Industry, **2**, 239 (1904); Schnabel-Louis "Handbook of Metallurgy," II, 1907 Ed., p. 546).

An objection to the use of acid electrolytes for detinning tinplate scrap is that iron also dissolves, which contaminates the electrolyte and produces impure tin. Iron stands higher than tin in the E. M. F. or solution pressure series in acid solutions. The current efficiency of acid tin salt electrolytes is less than either neutral or alkaline electrolytes not only on account of iron also dissolving, but because hydrogen is deposited with the tin in acid electrolytes (Bertram Blount, "Practical Electrochemistry," 1906 Ed., p. 126).

8. Mennicke received German patent 152,989 and English patent 25,550 for a process of recovering tin from tin-containing materials by the use of an electrolyte composed of tin chloride, ammonium chloride or other ammonium salt and an organic salt or organic acid. The treatment is best conducted at a temperature not less than 50° C. The electrolyte becomes altered by use, and the organic salt or acid is decomposed, so the solution must be regenerated after it has been in use (Metallurgie, **1**, 321 (1904)).

9. Borchers proposed the recovery of tin from tin-plate scrap by the employment of an electrolyte containing from 12 to 15 percent of sodium chloride and 3 to 5 percent of sodium stannate, electrolyzing at a current density of 50 to 150 amperes per square meter (4.6 to 14 amperes per square foot), potential of 2 to 3 volts, and temperature of 40° to 50° C. The tin will be deposited under these conditions as a non-adherent precipitate, which may be collected, washed, dried, melted and cast. Iron cells may be used (Schnabel-Louis, "Handbook of Metallurgy," II, 1907 Ed., p. 544).

10. Kendall was granted United States patent 656,982 for the use of electrolytes composed of alkali or alkaline earth nitrates for detinning tin-plate scrap. Fresh nitrate to be added from time to time in order to replace that which is changed to nitrite and ammonia (Zeitschrift für Elektrochemie, **7**, 37 (1912)).

Burgess removed tin from tin-plate scrap by using an electrolyte of sodium nitrate and making the tin-plate scrap the anode. It is stated that the stripping was accomplished in about three minutes (Electrochemical Industry, **2**, 10 (1904)).

11. German patents 20,303 and 184,023 were received by Luckow for a process of recovering tin from tin-plate scrap, alloys and metallurgical products by making the material the anode in an aqueous solution of fluorine compounds, such as the fluorides of potassium, sodium, ammonium, zinc, etc., either singly or a mixture of two or more. The solution may be acid or neutral. If the metallurgical product or the alloy contains silver, the silver will be recovered in the anode sludge (Elektrochem. Zeitschrift, **14**, 27 (1908)).

12. The most important electrolytic process for the detinning of tin-plate scrap is that which employs a caustic soda electrolyte. The first patent for the use of an alkaline bath for this purpose was granted in 1885 to Beatson, who received British patents 11,067 and 12,200 (Electrical Review, **44**, 939 (1904); Electrochemist and Metallurgist, **4**, 52 (1904)). The tin scrap was placed in an iron basket, and made the anode in a hot caustic soda electrolyte (sp. gr. 1.21), and the tin deposited on thin sheet iron cathodes. It is stated that the solution must be operated hot, in order to increase the electrical efficiency and to

prevent the rapid absorption of carbon dioxide from the atmosphere. The tin deposited as an amorphous metallic sponge; it was collected, pressed into cakes, and these cakes made the anode in a concentrated electrolyte of either stannous chloride or stannous sulphate, using a revolving cylinder of iron, on which the crystalline deposit was pressed into a solid state by a pressure roller. The purified tin was stripped from the cylinder, melted and cast into bars (Electrochemical Industry, **2**, 370 (1904); Electrical Review, **44**, 939 (1904)).

Goldschmidt employed a hot caustic electrolyte for the recovery of tin. The electrolyte contained from 3 to 5 percent of caustic soda reckoned as Na_2O, 1 to 2 percent of Na_2O combined with tin as sodium stannate, and 1.5 to 3 percent of Na_2O as carbonates. The electrolysis was conducted at temperature of 60° to 70° C., the tin being electrically dissolved, whereas the iron is passive (Zeitschrift für Elektrochemie, 1902, pp. 315, 357, 381; Electrochemist and Metallurgist, **1**, 32 (1902); Schnabel-Louis, "Handbook of Metallurgy," 1907 Ed., II, 547; Louis, "Metallurgy of Tin," 1911 Ed., 135; Allmand, "Applied Electrochemistry," 1912 Ed., 288).

Electrolytic detinning is conducted commercially in Italy, using a hot electrolyte of sodium hydrate. The tin scrap is placed in iron wire baskets between sheet iron cathodes in an iron tank. The tin deposits as a non-adherent sponge, which is collected, washed, pressed into cylinders, then reduced by melting with pulverized coke and a flux, and cast into bars which contain an average of 98.5 percent of tin. The impurities are principally iron, lead and copper. The detinned scrap is washed and sent to a steel mill. The best results of detinning are obtained by operating at a temperature between 60° and 80° C., with current density of 6 to 9 amperes per square foot, and E. M. F. of 2 to 3 volts, which gives a current efficiency of 75 to 90 percent. The electrolyte is heated by means of steam passing through iron coils in the tank. The most favorable concentration of the electrolyte was found to be from 10 to 12 percent of total alkalinity, the free alkali not exceeding 7 percent, the carbonates less than 3 percent, and the sodium stannate under 5 percent. The concentration of the electrolyte is properly maintained by removing a portion at intervals and replacing by fresh solution. The removed

portion is regenerated by saturating it with carbon dioxide under pressure and heating, which precipitates the tin as stannous hydroxide and hydrated stannic acid, and the iron and lead as carbonates. By this treatment the caustic soda is converted into bicarbonate and carbonate of soda. The precipitate is collected and treated for its tin content, and the filtrate converted into sodium hydroxide by adding lime, heating it, and filtering off the calcium carbonate. The regenerated solution of sodium hydroxide is reused for detinning (Metallurgical and Chemical Engineering, **10**, 202 (1912)).

According to Goldschmidt the electrolytic detinning process which employs an electrolyte of caustic soda is attended with many difficulties, the chief of which are the rapid absorption of carbon dioxide from the atmosphere, the trouble of keeping the solution hot, the loose manner in which the scrap must be packed so that the electrolyte may have free passage in order to dissolve effectively the tin, and the contamination of the electrolyte by iron, lead, soap, resin and carbonates. In the latter case the iron and lead are taken into solution as the result of chlorides in the electrolyte, and the collection of soap and resin is due to the grease and resin on old tin cans when detinned (Electrochemical and Metallurgical Industry, **3**, 434 (1905); Borchers-McMillian, "Electrolytic Smelting and Refining," 1904 Ed., 455; Metal Industry, **17**, 820).

Mennicke, reporting on electrolytic detinning in caustic electrolytes, states that the amount of free sodium hydrate and the temperature (best at 70° C.) of the electrolyte have great influence on the results of tin recovery. Carbon dioxide from the atmosphere reduces the conductivity of the electrolyte and causes the precipitation of tin hydroxide on the scrap, which interferes with the dissolving of the tin (Zeitschrift für Elektrochemie, **8**, 315, 357 and 381 (1902); Mineral Industry, **11**, 235).

Gelstharpe found that when new tin-plate scrap was made the anode in caustic soda electrolyte (sp. gr. 1.05) at temperature of 80° C., the tin did not dissolve, but became coated with a thin light brown film of high resistance, and that gases were liberated at the electrodes, causing high voltage and the passage of a relatively small amount of current. He found that by reversing the current for a moment, and then again making the tin plate

the anode, complete stripping of the tin was accomplished within a few minutes. During the dissolving of the tin the voltmeter registered about 1 volt, but as soon as the stripping was completed the potential increased to over 2.5 volts. Old pieces of tin plate which are tarnished are attacked immediately the current is switched on, and are quickly stripped. It was also noticed that when the cathode was agitated the tension required for the stripping was about 0.5 volt, which was a reduction of 30 to 40 percent of the electrical energy consumed (Transactions of the Faraday Society, **1**, 111 (1905)).

Gelstharpe favors the caustic electrolyte for detinning, giving the following reasons: Iron apparatus may be used; the electrolyte may be continually regenerated; the iron plate is not attacked. The deposit from the caustic electrolyte is an amorphous sponge, whereas the deposit formed in an acid electrolyte is composed of small dense crystals. The acid electrolyte is superior to the alkaline when the tin deposited is to be used as tin paste, which is a product used for silvering paper and for making ornamental paint (Transactions of the Faraday Society, **1**, 112 (1905); Electrochemical and Metallurgical Industry, **3**, 67 (1905)).

One objection to the alkali electrolyte for detinning is that it does not recover the tin from the iron-tin alloy at the surface junction of the two metals. The detinned scrap will contain as much as 0.2 percent of tin. Detinning in caustic electrolytes recovers from 90 to 95 percent of the tin on the scrap (Electrochemical and Metallurgical Industry, **3**, 67 (1905)).

13. Keith received United States patent 176,658, in 1876, for a process of recovering tin by the use of an electrolyte composed of caustic soda and sea salt. This process was employed commercially and with success, but was abandoned on account of the difficulty and expense of obtaining the material to treat. The cell was made of iron, the walls of which served as the cathode, on which the tin was deposited as sponge (Electrochemical and Metallurgical Industry, **7**, 79 (1909); Schnabel-Louis, "Handbook of Metallurgy," 1907 Ed., 545).

14. Borchers' electrolytic stannate process of detinning is the use of a hot caustic electrolyte containing about 10 percent of sodium hydrate and 5 percent of sodium chloride. This electrolyte is not very satisfactory, as it also dissolves iron, causing

reduction in the current efficiency, contamination of the solution, and production of impure tin (Zeitschrift für Elektrochemie, **7**, 34 (1912); Journal Soc. Chem. Ind., **16**, 42 (1897)).

15. Matthews, Heath and Davis used a hot electrolyte containing caustic potash and protochloride of tin for detinning scrap. They were granted United States patent 715,281 for a specially constructed cell for use in applying their process (Electrochemical Industry, **1**, 190 (1902)).

16. Walbridge made use of a solution of caustic soda and sodium nitrate for the electrolytic recovery of tin (Schnabel-Louis, "Handbook of Metallurgy," II, 1907 Ed., 545).

17. Beatson was granted English patent 11,067 for an electrolytic detinning solution which contains caustic soda and potassium cyanide. This electrolyte did not prove satisfactory on account of the decomposition of cyanide during the electrolysis (Schnabel-Louis, "Handbook of Metallurgy," II, 1907 Ed., 544).

18. Claus proposed the use of an electrolyte of sodium sulphostannate (sp. gr. 1.07) for detinning, the operation to be conducted at a temperature of 90° C., with current density of 10 amperes per square foot (Electrochemical Industry, **2**, 370 (1904); Electrical Review, June 18, 1904).

Leitch received several patents for special apparatus to be used for electrolytic detinning of tin-plate scrap. United States patents 843,616 and 859,566 are for apparatus; United States patent 906,726 is for a mechanical appliance for removing the detinned scrap and the precipitated tin from the cell; and United States patent 907,061 is for a method of heating and circulating caustic electrolytes so as to prevent the formation of carbonates (Electrochemical and Metallurgical Industry, **5**, 130 (1907), and **7**, 124 (1909)).

Detinning by Combination Chemical and Electrolytic Methods.

1. Nodin received French patent 386,499, German patent 199,729, English patent 7,706, Spanish patents 43,070 and 43,071, and United States patent 940,471 for a process of recovering tin from tin-containing materials by subjecting it to the action of a sulphuric acid solution of stannic sulphate or chloride containing an alkaline stannic halide salt, such as ammonium stannic chloride, at a temperature of approximately 40° C. The tin is

taken into solution as ammonium stannous chloride, with the reduction of an equivalent of stannic tin, whereas if lead is present it is not dissolved. The tin is recovered from the solution by electrolyzing between graphite anodes and sheet tin cathodes in a diaphragm cell, using current density of 9.3 to 18.6 amperes per square foot (1 to 2 amperes per square decimeter). In case the tin deposits as a non-adherent mass it may be pressed into cakes, made anodes in a second cell containing pure electrolyte, and be redeposited as adherent pure metal. During the electrolysis of the first solution, which was used for treating the tin-containing material, it is simultaneously regenerated for subsequent reuse by conducting the electrolysis in a diaphragm cell, depositing an amount of tin equivalent to that which was taken into solution, at the same time converting an equivalent into the stannic condition. The regenerated solution is then ready for treating another lot of material (Metallurgical and Chemical Engineering, **8**, 49 (1910); Metallurgie, **5**, 555 (1908)).

2. Reinders was granted German patent 245,682 for a process and apparatus for recovering tin from tin-plated ware, alloys and tin-plate scrap which consists in making the material the anode in an electrolyte of acid stannic and stannous chloride, ammonium chloride and ammonium sulphate. The tin is dissolved both chemically and electrochemically in this solution, and if lead is present it collects in the anode sludge as sulphate, oxide and dioxide. The end of the detinning is apparent by a sudden increase in potential, which may amount to 3 volts. The acidity of the electrolyte and the tin content are properly maintained by continually circulating the electrolyte through a second tank, which is provided with diaphragmed compartments and graphite anodes. By proper regulation of the current density relation in the two tanks the tin content can be held constant and the proportion of stannic to stannous salt be maintained. It is claimed that the deposit can be formed free of sponge by keeping the electrolyte in proper condition (Zeitschrift für Elektrochemie, **18**, 790 (1912); Metallurgie, **9**, 492 (1912)).

3. Bergsoe recovered tin from tin-plate scrap by treating it with an acid solution of stannic chloride, which is an energetic solvent for metallic tin, it being reduced to stannous chloride by the metallic tin which goes into solution as stannous chloride.

The resulting stannous chloride solution is then transferred to an electrolytic tank provided with graphite anodes and separated from the sheet tin cathode by means of a porous diaphragm. An amount of tin equivalent to that which was taken into solution is deposited, and the remainder is oxidized to the stannic condition. The regenerated solution is used for treatment of a new lot of material. The chief objections to the process are the slow rate of working and the gradual fouling of the solution by iron chloride, the latter causing heavy losses of chlorine so that every time the solution is reused the efficiency of stannic chloride is reduced by the amount of iron dissolved. English patent 7,026 was granted to Bergsoe for the process (Electrochemist and Metallurgist, **1**, 80 (1901), **2**, 8 (1902); Journal Society Chemical Industry, **24**, 12 (1905); Zeitschrift für Elektrochemie, **13**, 49 (1906); Allmand, "Applied Electrochemistry," 1912 Ed., 288).

4. United States patent 704,675 was issued to Brown and Neil for a method of detinning by means of a boiling acid solution of ferric chloride, which dissolves the tin as stannous chloride in equivalent to the amount of ferric chloride which is reduced to ferrous condition. Ores may also be treated in the same manner. The solution is then electrolyzed in the cathode compartment of a diaphragm tank, using graphite anodes and tin-plate cathodes. The ferrous and stannous solution is run steadily into the cathode compartment, and the ferric solution which is produced at the anodes is withdrawn and used for treatment of the tin-containing materials. The diaphragm is sufficiently porous so as to allow the solution to percolate from the cathode compartment to the anode compartment as rapidly as added. The chief drawback to the process is the unavoidable dissolving of much iron (Electrochemical Industry, **1**, 30 (1902); Journal Society Chemical Industry, **24**, 121; Allmand, "Applied Electrochemistry," 1912 Ed., 288).

5. Hemingway received English patent 8,759 and United States patent 791,555 for the use of a solution of ferric sulphate for detinning purposes. The material is treated with the hot solution, which dissolves the tin, forming stannous sulphate with the reduction of an equivalent of ferric to ferrous sulphate. The solution is electrolyzed, using iron anodes and sheet tin-plate

cathodes. When most of the tin is precipitated the solution is transferred to another vat and oxidized to ferric condition by means of nitre and heating (Journal Society Chemical Industry, **24**, 740; Electrochemical Industry, **3**, 309 (1905)).

Electrolytic Treatment of Tin Ores.

1. Snelling reduced cassiterite by placing it in contact with the cathode in an electrolyte of either hydrochloric acid, sulphuric acid, sodium hydrate or sodium stannate. During electrolysis the cassiterite is reduced by the liberated hydrogen, yielding a mass of impure tin. The reduced tin is collected, made the anode in a suitable electrolyte, and deposited as pure metal (United States patent 917,176).

2. Several German patents have been granted for the treatment of tin ores and slags which are based on the fusion of the material with caustic soda, leaching out the sodium stannate with water, and finally depositing the tin by electrolysis, using iron anodes and tin-plate cathodes, with solution at about 60° C. (Schnabel-Louis, "Handbook of Metallurgy," II, 1907 Ed., 543 and 544). In case the ores contain arsenic, antimony or sulphur, they must undergo roasting before they are fused with the caustic soda. These processes have failed not only on account of the cost of treatment, but also because the anode in a sodium stannate electrolyte becomes coated with a film of tin oxide which interrupts the flow of the current (Elektrochem. Zeitschrift, **5**, 168).

3. Vortmann and Spitzer obtained German patent 73,826 for a method of treating tin ores. The process is based upon the formation of soluble sodium sulpho-stannate by fusing the pulverized ore with a mixture of two parts of soda ash and one part of sulphur. The fused mass is then leached with water, an ammonium compound added to the solution, and the tin precipitated by electrolyzing at temperature of about 60° C., using lead anodes and tinned sheet cathodes. The process, even though successful in the laboratory, failed commercially on account of no cheap material being available which would withstand the corrosive action of fused sodium sulpho-stannate, and also because of the great loss of tin by volatilization (Zeitschrift für Elektrochemie, **1**, 19 (1894); Schnabel-Louis, "Handbook of Metallurgy," II, 1907 Ed., 543).

4. Thirot received the following patents for a process of treating ores, slags and tin-containing materials by leaching with a hot solution of sodium hydrate and sodium sulphide: French patents 364,589 and 386,499, German patent 203,519, British patent 28,342, Austrian patent 34,153, Belgian patent 196,428, Italian patent 86,438, and United States patent 883,589 (assigned to Mage). The pulverized material is leached with a hot solution containing from 10 to 12 percent of sodium hydrate and some sodium sulphide, at temperature of 80° C., which will take into solution from 4 to 5 percent by weight of tin. The presence of the sodium sulphide prevents the dissolving of base metals. The tin is deposited from the solution by electrolyzing at 80° C., using iron anodes and sheet tin cathodes, with current density of 28 to 37 amperes per square foot (300 to 400 amperes per square meter). When the tin has been reduced to about 1 percent the solution is again used for extracting a fresh lot of material. It is stated that an electrolyte containing sodium hydrate, sodium stannate and sodium sulphide may be used advantageously for refining impure tin, from which the tin is deposited as an adherent mass of pure metal (Elektrochem. Zeitschrift, **15**, 78; Metallurgie, **6**, 64 (1909)).

Other methods have been patented for leaching tin ores with aqueous solutions of either sulphuric acid, hydrochloric acid, sodium bisulphate or acid ferric chloride, and, after leaching, subjecting the resulting solution to electrolysis for the recovery of the tin. The methods, when tried on a commercial scale, proved unsuccessful (Schnabel-Louis, "Handbook of Metallurgy," II, 1907 Ed., 544).

V. ELECTROLYTIC REFINING OF TIN.

On account of the ease and comparative cheapness of refining tin by liquation methods (M. P. of tin = 232° C.) and by oxidation methods, electrolytic refining has little promise of being commercially employed.

Practically the only ore of tin is cassiterite (SnO_2; Sp. Gr. = 6.8 to 7.1; when pure it contains 78 percent tin), which is found associated with such minerals as quartz, feldspar, and mica in the form of granite or gneiss gangue. In some localities cassiterite is also accompanied by metalliferous minerals such as pyrite,

arsenopyrite, chalcopyrite, wolframite and molybdenite. These minerals, with the exception of wolframite, may be separated by water concentration methods. A recently developed method for separating wolframite, in case pyrite is also present, consists in calcining to the magnetic condition then subjecting the pulverized ore to magnetic separation, the pyrite and the wolframite being removed. (Schnabel-Louis, "Handbook of Metallurgy," II, 1907 Ed., p. 478; Louis, "Metallurgy of Tin," 1911 Ed., p. 12).

Commercial tin contains from 0.5 to 1.5 percent of impurity, which is one or more of the following metals: zinc, iron, lead, bismuth, antimony, copper, arsenic, tungsten, molybdenum, silver. As there is no demand for very pure tin, and also because silver and gold are not present in quantity to pay for their recovery, electrolytic refining has, up to the present time, not been practised, except when very pure metal was wanted, or when experimental refining was conducted. The product which is produced by pyro-heat methods of refining is of sufficient purity for commercial purposes.

A number of electrolytic methods have been developed, the majority using electrolytes of the stannous salt. The efficiency of the refining is given for some of the electrolytes, the figures being obtained by using the factors for stannous solutions which are 0.6163 milligram per coulomb, 2.2188 grams per ampere-hour, 204.43 ampere-hours per pound; the factors for stannic solutions are 0.30817 milligram per coulomb, 1.1094 gram per ampere-hour, 408.86 ampere-hours per pound.

1. Brand conducted experiments on the electrolytic refining of tin, using an electrolyte containing 2.5 percent by volume of concentrated hydrochloric acid and 9 percent by weight of stannous chloride. The method did not find commercial application. (Schnabel-Louis, "Handbook of Metallurgy," 1907 Ed., II, p. 549; Dammer, Chem. Technology, II, 27 and 324).

2. Michaud and Delasson received French Patent 435,936 for the use of a tin electrolyte prepared by dissolving stannous chloride in water, adding sulphuric acid till the precipitated oxychloride dissolved, and then stirring into the solution about 1 percent of magnesium chloride and 1 percent of boric acid. The cell used for the refining is constructed with a sheet copper cathode

placed horizontally on the bottom, on which the tin crystals are deposited and removed by scrapers. (Journal Society Chemical Industry, **31**, 395 (1912)).

3. Mennicke conducted experiments on the electrolytic refining of tin in fluosilicate electrolytes, and obtained deposits which were similar to lead deposits produced under the same conditions of current-density and temperature. The electrolyte was prepared by dissolving freshly precipitated stannous hydroxide in hydrofluosilicic acid in proper proportions to give a solution containing 10 percent tin and 10 percent free hydrofluosilicic acid by weight. Tin oxide was found to be insoluble in hydrofluosilicic acid. The presence of free hydrofluoric acid was found not to interfere with the production of satisfactory deposits.

The electrolysis was conducted at 20° C., using current at density of 9.3 ampere per sq. ft. (1 amp. per sq. dm.) and an average of 0.4 volt. Distance between electrodes about 2 inches (5 c.m.) The tin deposited extremely solid and tough, even without the presence of any addition-agent such as gelatine or albumen. The lower the voltage the finer the crystals.

Better results were obtained by using pure tin anodes than with those of a tin alloy. The presence of lead finally caused the deposit to become spongy, but still the deposited tin was pure. He states that very pure tin can be produced, which is especially suited for preparing pure chemicals. (Elektrochemische Zeitschrift, **12**, 112, 135, 161 and 180 (1905); Zeitschrift für Elektrochemie, **12**, 112; Electrochemical and Metallurgical Industry, **4**, 26; Mineral Industry, **14**, 555; Betts, "Lead Refining by Electrolysis," 1908, p. 47).

Mennicke was granted U. S. Patents 779,091 and 779,092 for the process of electrolytically refining tin in stannous fluosilicate electrolytes.

4. Mention has been made that neutral concentrated solutions of either stannic chloride or stannous chloride can be used for producing pure tin, as these electrolytes yield a coarse crystalline deposit. (Neumann-Kershaw, "Electrolytic Methods of Analysis," 1898 Ed., p. 148).

5. Beautiful dense deposits of tin can be produced without the evolution of hydrogen at the cathode by electrolyzing a solution of sodium-stannous chloride with low current-density, and at

ordinary temperature. (Bulletin Soc. d'Enc. L'Ind. Nat., July, 1912, p. 28).

6. Quintaine was granted English Patent 5,496 for the deposition of pure tin by use of an electrolyte composed of stannic chloride, or stannous chloride, and an ammoniacal salt, preferably ammonium chloride. It is claimed that a perfect deposit of chemically pure tin was produced from this solution. The statement is made that "to obtain a clear solution, and one that will act as a good conductor of the current, the precipitate first formed on dissolving the tin salt in water is redissolved by the addition of ammonium chloride, and the solution filtered. The current should be weaker than that employed for the electrodeposition of copper, or the deposit will be irregular." (Journal Society Chemical Industry, **19**, 1121 (1900); Mineral Industry, **9**, 646).

7. Hollard prevented the formation of spongy deposits of tin by using an electrolyte composed of 12 grams of sodium stannate (Na_2SnO_3) and 200 grams of sodium sulphate per liter, and electrolyzing it at a temperature of 80° C. at current-density of 2 amperes per sq. ft. (0.2 ampere per sq. dm.). (Bulletin Soc. d'Enc. L'Ind. Nat., July, 1912, p. 28).

8. Fischer satisfactorily deposited tin by using a solution of ammonium sulpho-stannate to which was added a reducing agent such as sodium sulphite, sodium hyposulphite, or potassium cyanide. (Zeitschrift Anorg. Chemie, **42**, 363 (1904)).

9. Neumann received German Patent 198,289 for a process of obtaining pure dense deposits of tin by use of an electrolyte composed of an alkali sulpho-stannate, and operating at temperature of about 70° C. The presence of free alkali is said to be advantageous.

10. Claus refined tin in an aqueous solution of sodium sulpho-stannate, of sp. gr. 1.07, and at 90° C., employing current at 10 amperes per sq. ft. (1.1 amp. per sq. dm.). All the impurities except arsenic and antimony collected as anode sludge, principally as sulphides. Arsenic and antimony, when present, were precipitated on the cathode with the tin. He found that the cathode tin containing arsenic and antimony could be freed from these by making it an anode in an acid solution of sodium thiosulphate containing hydrochloric acid, the arsenic and antimony in this case remaining as sulphides in the anode sludge. The cathode

tin was melted and cast into bars. (Elektrochem. Zeitschrift, **8**, 168; Schnabel-Louis, "Handbook of Metallurgy," 1907 Ed., II, 549).

11. Patents have been granted to O. Steiner for a tin refining process, using an electrolyte similar to that published by Claus, as given above (10). The patents issued are: U. S. Patent 890,249; German Patent 193,528, English Patent 10,230, French Patent 374,116. The claims are that by using an electrolyte containing about 10 percent by weight of an alkali sulphide, to which has been added about 1 percent by weight of flowers of sulphur, tin of high purity (99.9 percent) can be produced as a dense smooth deposit, when the electrolysis is conducted so that the E. M. F. is kept below 0.2 volt, current-density under 4.5 amperes per sq. ft. (0.5 amp. per sq. dm.), and solution kept at about 90° C.

The electrolyte is prepared by dissolving commercial sodium sulphide in the necessary amount of water to produce a 10 percent solution, adding 1 percent by weight of flowers of sulphur, letting settle, then filtering. It is necessary to analyze the solution at intervals during the electrolysis, and to add sodium sulphide and flowers of sulphur so as to keep up the concentration. The loss of sodium sulphide will be due to oxidation and to the formation of sodium sulpho-stannate. The amount of tin in the electrolyte reaches a maximum of about 2.2 percent by weight, and remains constant thereafter so long as the concentration of sodium sulphide is kept proper.

One of the essentials in the use of this solution for refining tin is that the voltage must be kept below 0.2, and that the electrolyte be maintained above 90° C. If the potential is allowed to rise, gassing at the cathode occurs. At 0.6 volt violent liberation of hydrogen takes place, with decomposition of the electrolyte and at the same time the tin deposits as a dull spongy mass, which contains oxide.

The raw tin should not contain more than 10 percent of impurities, and the iron content should be below 2 percent, otherwise the anode sludge will adhere and cause the voltage to rise and produce gassing and a spongy deposit. The anode sludge will contain the iron, lead, antimony, copper, bismuth and silver.

Distance between the electrodes about 1⅜ inch (3.5 cm.). Iron tanks are most suitable.

The conditions which are given as being necessary to obtain high current efficiency and to produce dense, pure deposits are:

a. Temperature of electrolyte above 90° C.

b. Thorough and constant circulation, or mixing of electrolyte.

c. Voltage maintained below 0.2.

d. Pure plate cathodes (cathodes of iron, copper and lead cause the voltage to rise and the deposit to be non-adherent and spongy).

e. Pure electrolytes, free of arsenic, antimony, copper, etc.

f. Electrolyte containing 10 or more percent of sodium sulphide by weight. A more concentrated solution permits the use of higher current-density.

g. Add to the electrolyte about 1 percent by weight of flowers of sulphur just before placing a new lot of anodes in the tank. The sulphur is necessary to form sulphides with the impurities in the anode, thereby preventing the contamination of the electrolyte.

h. The electrolysis must not be interrupted until the anodes are to be removed. When the current is interrupted, gassing will occur when the current is switched on, and spongy deposit will form.

A means of maintaining the same current-density from a number of electrodes when placed in the same tank, was accomplished by soldering all of the anodes to the same supply conductor, and all of the cathodes to the negative conductor. When this was not done the voltage between all of the opposite electrodes was not the same.

The ampere-hour efficiency is given as above, 98.5 percent. It is also stated that "the deposit could be still improved by adding a colloid to the electrolyte, for example, gelatine as is used in the Betts' process for electrolytically refining lead." (Elektrochem. Zeitschrift, May, 1908; Journal Society Chemical Industry, **26**, 768 (1907); Electrochemical and Metallurgical Industry, **5**, 309 (1907)).

12. Sperry obtained U. S. Patent 874,707 for a process of refining tin by the use of a diaphragm cell. It is stated that electrolytes consisting either of sulphate, ammonium oxalate, ammonium sulphide, or of chloride, fluoride, or hydrofluoric

acid could be used in the cell. The impure metal to be electrolytically refined may be given a preliminary refining by fire-methods in order to remove the major portion of the impurities, then cast into anodes. The use of the diaphragm between the anodes and the cathodes is to prevent the cathode deposit becoming contaminated by floating anode sludge. The impurities which accumulate in the electrolyte as soluble salts are to be removed periodically by withdrawal of a portion of the electrolyte, and replacing it by fresh solution. Electrolytes work better when kept at 85° C. (Journal Society Chemical Industry, **27**, 343; Electrochemical and Metallurgical Industry, **6**, 76).

There are several articles, in themselves reviews, which could not be reviewed. They may be found in the following publications:

"Electrical Engineering," London, July 15, 1908. "The Electrolytic Refining of Tin, and Recovery of Tin from Its Ores," by Sherard Cowper-Coles.

"Electrical Review," **44**, 939 (1904). "Tin Scrap Recovery Processes," by J. B. C. Kershaw.

"Zeitschrift für Elektrochemie," **8**, 315, 357, 381 (1902). "Electrical Recovery of Tin from Tin-Plate Waste," by H. Mennicke.

"Zeitschrift für Elektrochemie," **12**, 245 (1906). "Progress in the Metallurgy of Tin, with Special Reference to Electrochemistry Since 1904" (1904 to 1906), by H. Mennicke.

"Elektrochem. Zeitschrift," **11**, 223, 245 (1904); **12**, 1, 27 (1905). "Progress in the Electrolytic Tin Stripping Industry Since 1902."

"Elektrochem. Zeitschrift," **13**, 49, 258 (1906-1907); **14**, 8, 25, 54, 77 (1907-1908). "Advances and Improvements in the Metallurgy of Tin, Especially in Electrochemistry During 1906," by H. Mennicke.

"Elektrochem. Zeitschrift," **15**, 78, 101, 123, 148, 173, 198, 224, 257, 274 (1908-1909). "Progress in the Metallurgy of Tin, with Special Reference to Electrochemistry During 1907," by H. Mennicke.

"Elektrochem. Zeitschrift," **16**, 292, 318, 351 (1909-1910). "Progress in the Metallurgy of Tin in 1908," by H. Mennicke.

VI. EFFECT OF ORGANIC ADDITION-AGENTS IN TIN ELECTROLYTES.

There should be little difficulty in obtaining thin, smooth, adherent deposits of tin; but when the deposition is carried to an appreciable thickness, difficulties arise. The electrodeposits of tin have a tendency to become crystalline and brittle, more and more so the longer the electrolysis is continued. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333).

The physical condition of electrolytically deposited metals is economically of the most importance, since the metallurgist, as well as the electroplater, wants a coherent, dense, smooth deposit, as the purity of the cathode metal depends upon its density and smoothness; and, besides, the ampere-hour efficiency of a refinery is dependent upon the prevention of short circuits between anodes and cathodes. As a rule, the rougher the cathodes the lower the ampere-hour efficiency and the less pure the refined metal.

The characteristic form of tin, deposited from acid electrolytes, is a mass of loose, non-adherent crystals. This tendency is less apparent in neutral and in alkaline electrolytes. The concentration of the electrolyte, the temperature of the electrolyte, and the current-density, each have an effect on the character of the deposit. In general, the more concentrated the electrolyte up to saturation, and the higher its temperature, the more coherent and smoother the deposit. Another factor influencing the deposition is one which is the result of the presence of certain organic addition-agents, which change the character of the deposit either beneficially or detrimentally.

The effect of addition-agents, when properly selected, is to cause the deposit to be smoother, denser, and more adherent. When not properly selected, the opposite effect may result—that is, the deposit will be more crystalline and less adherent, or collect as a spongy mass which drops from the cathode.

It has been found that the addition of glue or gelatine to certain tin baths, in the proportion of 1 part by weight to 1,000 parts of electrolyte, has a remarkable effect on the character of the deposited tin, and, at the same time, allows the use of a higher current-density. Other addition-agents which have been found to be beneficial for certain electrolytes are glucose, saccharine, acetone, and organic salts of aluminum and iron. The effect of

organic addition-agents is not permanent, so in all cases, when used, further additions must be made periodically. (Barclay and Hainsworth, "Electroplating," 1912 Ed., p. 333; Fields, "Principles of Electrodeposition," 1911 Ed., p. 215).

1. Hollis' U. S. Patent 916,155 is for the use of an electrolyte containing tin fluosilicate, and to which gelatine or glue is added for the purpose of increasing the density of the deposit. (Electrochemical and Metallurgical Industry, **7**, 224 (1909)).

2. German Patent 244,567, to Matuschek, is for an electrolyte consisting of a concentrated solution of ammonium oxalate saturated with tin-ammonium chloride ($SnCl_2.2NH_4Cl$), to which an addition of black-oak tannin (quercitrinic acid) has been added. The electrolyte which he used was prepared by dissolving 200 grams of stannous-ammonium chloride in 600 c.c. of a concentrated solution of ammonium oxalate, then the addition of 50 grams of black-oak bark tannin. This solution was electrolyzed at ordinary temperature, and a solid deposit of tin was produced, when current-density of 28 amperes per sq. ft. (3 amperes per sq. dm.) was employed. The statement is made that other additions may be made to the bath, such as sodium dihydrogen phosphate, sodium silicofluoride, an inorganic acid other than nitric acid, preferably hydrofluosilicic acid, or a mixture of borax and hydrofluosilicic acid. As an example of a bath of this composition, there was added, instead of 50 grams of tannin, to the bath given above, 6 grams of tannin and 6 grams of sodium dihydrogen phosphate. This bath was found to be more constant than the first.

Claims were made that much higher current-density can be employed and the electrolysis be conducted at ordinary temperature, and the deposited tin still form solid and adherent, which is not possible by using the generally-employed hot alkaline electrolytes. An E. M. F. of 2 to 3 volts was maintained between electrodes 13 cm. (5⅛ inches) apart, and good deposits continued to form.

The electrolyte is said to be suitable for the refining of tin, electroplating of tin, and electro-detinning of tin-plate scrap. The addition of ammonium salts, such as ammonium chloride, and organic substances, such as carbohydrates or gums, etc., is desir-

able for the production of brilliant deposits. (Metallurgie, **9**, 492 (1912); Journal Society Chemical Industry, **31**, 440 (1912); Zeitschrift für Elektrochemie, **18**, 790 (1912)).

3. Steiner found that tin deposited from sodium sulphostannate electrolytes (See Sect. V, 11) "could be still improved by adding a colloid to the electrolyte, for example, gelatine, as is used in the Betts' process for electrolytically refining lead."

4. E. F. Kern and A. P. Frapwell conducted experiments on the effect of certain organic addition-agents on the character of electrolytically deposited tin from solutions of sodium-stannous chloride, stannous fluoride, and sodium-stannous fluoride. (Results have not been previously published.) These salts were selected on account of their solubility, and because their solutions are highly ionized and are excellent conductors.

(a) In Sodium-Stannous Chloride Electrolyte.

The solution was prepared to contain about 80 grams of tin and 50 grams of sodium, as chlorides, per liter, by dissolving a calculated amount of sodium chloride in water, then adding a calculated amount of stannous chloride crystals. The electrolysis was conducted at ordinary temperature, using cast-tin anodes and tin-foil cathodes, with current-density of 10 amperes per square foot (1.1 amp. per sq. dm.). The distance between electrodes was about 1¼ inch (3 cm.), and potential about 0.1 volt. The deposit formed as a mass of bright needle crystals, which soon short-circuited the electrodes.

The effect of three addition-agents: gelatine, gum-arabic, and tannin was investigated, the electrolysis being conducted at the same temperature and current-density as above.

The presence of gum-arabic, in the proportion of 1 gram per 800 to 1,200 c.c. of solution, caused the deposit to form as small, bright, adherent crystals, which did not short-circuit the electrodes. The electrolysis was conducted for periods of 1 to 3 hours. The gum-arabic was added as an aqueous solution. It did not cause a precipitate to form when it was added to the electrolyte.

The addition of a solution of gelatine, and of tannin, caused a white collodial precipitate to form when added to the electrolyte. The deposits formed from electrolytes, to which the gelatine and the tannin were added in the proportion of 1 gram per 500 to 1,500 c.c. of electrolyte, were à mass of small bright needle crystals which could be rubbed off with a stirring rod. These two addition-agents caused the tin to be deposited as very small needles, whereas the deposits formed in the solutions which contained no addition were long dendritic needles.

(b) In Stannous Fluoride Electrolyte.

The solution was prepared by dissolving a weighed amount of stannous chloride in a small volume of water and adding a few c.c. of hydrochloric acid to clear the turbidity. The tin was then precipitated by the addition of a concentrated solution of sodium carbonate, which gave a precipitate of stannous hydroxide. This was washed free of alkali by decantation, and finally filtered. It was dissolved in moist condition in a measured quantity of 40 percent hydrofluoric acid, to give a solution containing a very slight excess of acid. This concentrated solution was diluted, so as to contain about 80 grams of tin per liter.

The electrolysis was conducted at ordinary temperature, using wax beakers for the cells, and cast-tin anodes and tin-foil cathodes. The current was passed at 10 amperes per square foot (1.1 amp. per sq. dm.), with the electrodes about 1½ inches (3.8 cm.) apart, and E. M. F. of 0.15 to 0.16 volt. The electrolysis was carried on for periods up to 8½ hours.

The deposits formed, with no addition-agent present, as a mass of loosely adherent sparkling dendritic needles, which soon caused short-circuiting. The anodes were evenly corroded, and remained very bright throughout the electrolysis.

The addition-agents tried were solutions of tannin, gelatine, gum-arabic, glycerine, resorcine, saccharine, grape-sugar, and glucose. The deposits were not much altered by any of the addition-agents except tannin, gum-arabic, resorcine and glucose. Tannin proved to be the most effective, and resorcine and glucose less

effective than either the tannin or gum-arabic. The additions were made in small amounts of the aqueous solutions at a time, the first addition being in the proportion of 1 gram per 2,000 c.c. of electrolyte, then 1 gram per 1,500 c.c. of electrolyte, and so on by a 500 c.c. decrease in the proportion of the electrolyte, until finally 1 gram of the addition-agent per 100 c.c. of the electrolyte had been added.

In the case when tannin was used, 1 gram per 1,500 c.c. of electrolyte caused the deposit to form finely crystalline and adherent. The best deposits formed when tannin was present.

The presence of gum-arabic in the proportion of 1 gram per 1,500 c.c. electrolyte caused a marked improvement in the deposition. Larger proportions did not prove beneficial. In no case was a dense smooth deposit formed.

With resorcine and glucose, not much improvement resulted until they had been added in the proportion of 1 gram per 100 c.c. of electrolyte, and even then the crystalline deposition was not restrained.

(c) In Sodium-Stannous Fluoride Electrolyte.

This electrolyte was prepared in the same manner as the stannous fluoride electrolyte, with the addition of sodium fluoride. The solution contained 80 grams of tin and 50 grams of sodium in the form of fluorides.

The electrolysis was conducted at room temperature (20 to 23° C.) in the same manner as the stannous fluoride electrolyte, but in this instance operating at current-density of 15 amperes per square foot (1.6 amp. per sq. dm.). The electrodes were placed 1¼ inches (3 cm.) apart, and the E. M. F. averaged 0.18 volt. The deposits formed as bright dendritic needles, which soon short-circuited the electrodes.

The same additon-agents were used as for the stannous fluoride electrolytes, they being added at regular intervals in small amounts at a time, until an apparent change in the characteristic appearance was noticed.

Tannin in the proportion of 1 gram per 2,000 c.c. of electrolyte caused the deposition of a smooth, very crystalline, firmly

adherent coating. The run was continued for periods of 6½ hours. The anodes corroded evenly and remained bright. The potential between electrodes varied from 0.24 to 0.26 volt. Current-density of 15 amperes per square foot (1.6 amp. per sq. dm.).

Gelatine in the proportion of 1 gram per 1,000 c.c. electrolyte caused the deposit to form as adherent small crystals, with a few small dendrites on the edges of the cathode. It is not so satisfactory an addition-agent as tannin. Current at 15 amperes per square foot (1.6 amp. per sq. dm.), and voltage of 0.24 to 0.26. Time of run, 6½ hours. The addition of a larger proportion of gelatine caused the electrolyte to assume a milky appearance, due to a chemical precipitation.

Gum-arabic, in the proportion of 1 gram per 1,500 c.c. electrolyte, gave a deposit which was smooth and adherent, and was composed of very fine crystals, similar to the deposit formed by the presence of gelatine. Solution remained clear. Time of run was 6½ hours. E. M.F. varied from 0.24 to 0.27 volt. The presence of 1 gram of gum-arabic per 750 c.c. of electrolyte caused the deposit to form dark, spongy and non-adherent.

The addition of resorcine in all proportions between 1 gram per 1,500 c.c. and 750 c.c. of electrolyte caused the deposit to form as small adherent crystals instead of needle crystals. The deposits in no instance were satisfactory, as the crystals could be scraped from the cathode by means of a spatula. Time of run, 6½ hours. E. M. F. between electrodes was 0.23 to 0.25 volt. The voltage was lower in this case on account of the crystals on the edges of the cathode reducing the distance between it and the anode.

Saccharine, glycerine, grape-sugar, and glucose added in proportions up to 1 gram per 500 c.c. of electrolyte did not in any case have any marked effect on the character of the deposit.

Lead cathodes were used at one time, instead of the tin-foil, and it was found that the deposits formed on the lead cathodes were in every instance more crystalline and less adherent than when tin-foil cathodes were used.

It was also observed that the beneficial addition-agents caused

an increase in the potential of from 0.01 to 0.05 volt. This, no doubt, is evidence that there is an interference with the ionization of the cations about the cathode, by the presence of the organic addition-agent. It would be of much interest to have physico-chemical explanation of the effect of certain addition-agents on the character of cathode deposits, and a reason for the increase of potential.

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THE ELECTRODEPOSITION OF COPPER

By C. W. Bennett.

The number of solutions which may be used for the deposition of copper is very great. These solutions, however, fall into three general classes: First, acid solutions of the ordinary copper salts; second, alkaline solutions of complex salts. To these solutions certain substances may be added to improve the character of the deposit. As a third class, therefore, these solutions with "addition agents" may be considered. The solutions in these classes which are said to give good deposits of copper will be given in the order outlined above.

Acid Solutions.

The most important solution is the acid sulphate. This may contain[1] 5 percent to a saturated solution of $CuSO_4.5H_2O$, 1 to 16 percent H_2SO_4. A large number of these solutions of varying concentrations might be given, but this seems hardly necessary, since the effect due to change of concentration is not marked. The copper sulphate solutions used are generally acid, the acid dissolving impurities[2] such as oxides, hydroxide or basic salts.

[1] Oudry: U. S. Pat., 22,132.
Farmer: U. S. Pat., 426,788.
Elkington: U. S. Pat., 100,131, 101,009, 242,338, also 326,760.
Bancroft: Trans. Am. Electrochem. Soc., **4**, 55 (1903).
Schwab and Baum: Jour. Phys. Chem., **7**, 493 (1903).
Langbein: Handbuch der Elektrolytischen Metallniederschläge, 5th Ed., Leipzig (1903). Translated by Brannt: Electrodeposition of Metals, 3rd Ed., Henry Carey Baird & Co., Philadelphia (1898).
Fontaine: Electrolyse, 2nd Ed., Baudry et Cie Paris (1892).
Pfanhauser: Monographien über angew. Elektrochemie, **5** (1903); **11** (1904).
Elektroplattierung, Galvanoplastik u. Metallpolierung, 4th Ed. (1900).
Watt and Philipp: Electroplating and Refining of Metals, D. Van Nostrand Co., New York (1902).
McMillan: A Treatise on Electrometallurgy, 2nd Ed., Charles Griffin & Co., London (1899).
Borchers: Electrometallurgie, 2nd Ed. (1896). Translation by McMillan: Electric Smelting and Refining, Charles Griffin & Co., 2nd Ed. (1904).
Phil. Mag. (4), **1**, 41 (1871).
Ulke: Modern Electrolytic Copper Refining. John Wiley & Sons, 1st Ed. (1903).
Monographien über angew. Elektrochemie, **10** (1904).

[2] Bancroft: Trans. Am. Electrochem. Soc., **9**, 223 (1906).
Jour. Phys. Chem., **9**, 277 (1905).

Above 1 or 2 percent acid the character of the deposit is not markedly changed by increasing the acid concentration. The current density should be about 1.5 to 2.5 amperes per sq. dm. of cathode surface with 15 percent copper sulphate and 6 percent sulphuric acid, without stirring. The deposit can be made much smoother, of higher strength and therefore finer grained by rapidly rotating[3] the cathode or by increasing the current density, which may be done if the solution be stirred well. The beneficial action of rotation of the cathode and an increase of current density is general, but, since the interest is in the composition of solutions primarily, this will not be referred to again. Porous copper[4] is obtained at a high current density without stirring.

For electrotyping, the solution[5] generally contains less acid than otherwise, some baths being recommended which contain no acid. The current density used must be above a definite minimum, for below this cupric ions only are reduced to cuprous,[6] which by hydrolysis form cuprous oxide. When the current density is increased the cuprous ions are also reduced directly to metallic copper, and consequently the hydrolysis of the cuprous ions becomes negligible. It is claimed[7] that the current density may be higher in neutral than in acid solutions, as is shown below.

Solution, Percent		Amperes per Sq. Dm.	
$CuSO_4 \cdot 5H_2O$	H_2SO_4	Minimum	Maximum
15	0	2.6	3.9
15	6	1.5	2.3
20	0	3.4	5.1
20	6	2.0	3.0

[3] Elmore: U. S. Pat., 464,351; Electrochemist and Met., 3, 151 (1903); Electrochem. and Met. Ind., 3, 83 (1905).
Lloyd: U. S. Pat., 636,212.
Borchers, p. 209.
Cowper-Coles: U. S. Pat., 644,029 and 895,163; Electrochemist and Met. 3, 244 (1903).
Electrochem. and Met. Ind., 6, 412 (1908); Min. Ind., 9, 229 (1900).
Bennett: Trans. Am. Electrochem. Soc., 21, 253 (1912).
Jour. Phys. Chem., 16, 294 (1912).

[4] Zeit. Elektrochemie, 3, 130 (1896).

[5] McMillan: *l. c.*, Langbein: *l. c.*
Pfanhauser, Monographien ü. angew Elektrochemie, 11, 36 (1904).

[6] Foerster: Zeit. Elektrochemie, 3, 480 (1896).

[7] Langbein: p. 504.
Brannt: p. 363; Mon. ü. angew. Elektrochem., 5, 6 (1903).

With the higher current density allowable, smaller crystals and therefore a harder deposit would be obtained, which is important in electrotyping. This allowable increase in current density must be due to the fact that impoverishment of copper ions is less in neutral than in acid solution, with the same current density. This would be occasioned by the fact that in the acid solution the hydrogen ions carry part of the current, and are therefore transferred to the cathode. In the neutral solution the copper ions carry all of the current and are transferred to the cathode, in place of the hydrogen in acid solutions. Relatively more copper ions being carried in, more may be deposited from unit surface in unit time, in the neutral solution, before impoverishment is sufficient to spoil the deposit. In other words, a higher current density can be used in neutral than in acid solutions. The neutral solution seems to be opposite from what should be used, for the acid solution gives smaller crystals, and hence a harder deposit, which should be desirable for electrotyping. The increase in current density, however, may offset this tendency.

For plating iron by immersion the solution[8] is a dilute one, about 1.5 percent copper sulphate and 1 percent sulphuric acid. It may also be a neutral concentrated solution[9] of copper sulphate.

The acid nitrate solution so widely used in analysis, so far as is known, is not used in plating. A solution of copper and ammonium nitrate has been suggested,[10] however. This may contain from 100 to 250 grams of ammonium nitrate in 4 liters of water. This solution is then used in forming the bath by electrolysis with a copper anode until the deposit is as desired. There is claimed a wide limit for the current density. It is claimed that the conductance of this solution is better than that of the sulphate, the character of the deposit approaching that from the cyanide solution, without the evolution of dangerous fumes. The cost, as well as the more important facts that the efficiency is low and that conditions of concentration cannot be as widely varied as in the case of the sulphate, has prevented wide use of the nitrate solution.

[8] McMillan: p. 138; also Langbein, p. 491.
[9] Brannt: p. 358.
[10] Farmer: U. S. Pat., 319.687.

Gauduin's[11] solution consists of a solution of copper oxalate and ammonium oxalate with an excess of oxalic acid. The concentration of this solution is not at hand. It is claimed, however, that the solution at about 55° C. gives a good deposit. This solution is acid, but is intermediate between the straight acid solutions and the alkaline baths, where the copper forms part of a complex ion.

The following solutions[12] have been studied with reference to the character of the deposit:

TABLE I.

Solution	Composition	Grams of Copper Salt per Liter of Solution
A	Copper Sulphate acidified with H_2SO_4	258
B	Copper Nitrate acidified with HNO_3	352
C	Copper Potassium Cyanide with excess of KCN	47
D	Cupric Acetate acidified with Acetic Acid . . .	5
E	Copper Am. Chloride acidified with HCl	. .
F	Copper Am. Sulphate acidified with H_2SO_4 .	41

These solutions with varying current densities show that the deposits upon stationary electrodes show irregularity after a time, which is shown in Table II.

TABLE II.

Solutions	Current Density, Amperes per Sq. Dm.					
	1.1	2.2	4.4	8.8	17.6	35.2
	Number of Hours Deposition before Deposit Shows Irregularity					
A	. . .	40	25	8	.	. .
B	. . .	.	50	40	30	5
C	30	20	8	2		. .
D	45	30	25	8	. .	. .
E	50	40	25	5	. .	. .
F	45	30	20	5	. .	

From this behavior it might be assumed that the acid nitrate solution was the best one for the purpose of plating. This acid exercises a stronger solution effect on impurities as well as upon

[11] Langbein: p. 310; Brannt: p. 231; Electrochemist and Met., 3, 255 (1903); Fontaine: p. 140.

[12] Beadle: Electrochemist and Met. 1, 163 (1901).

the metal itself. The metal tends to be obtained purer, therefore, than otherwise. The corrosion of the copper being greater, the voltage difference between cathode and solution is greater. This increase in voltage represents an increase in the work required to deposit a given amount of the metal, since the current is constant. This increase in work may be considered as spent on the metal in the nature of working and thereby decreasing the crystal size. The deposit will therefore be of finer texture with the nitrate solution. This is general; the higher the voltage between cathode and solution, the finer will be the crystals.

Alkaline Solutions.

Copper plating is widely used as a basis for nickel plating on iron, steel and such metals. The object here is to obtain a thin, smooth coating over the surface of the metal, of such a nature that the iron will not be dissolved by and contaminate the nickel solution. In order that this copper be deposited by the current a solution must be used in which iron does not replace copper. For this an alkaline solution is used. Where the primary object is copper plating, after receiving a preliminary coating the piece to be plated is placed in an acid bath, where the deposit is thickened up. When copper plating is used as a basis for other plate the alkaline bath is of greater importance than the acid one.

In all of these solutions copper tends to dissolve with readiness. Since the concentration of copper ions in these solutions is very low it follows that the potential between the electrode and the solution is greater than that between copper and acid solutions. This gives rise to finer crystals, as was stated above, and therefore a finer-textured deposit from alkaline than acid solutions.

The solutions used in practice contain from

50 to 80 grams of copper carbonate
60 to 100 grams of potassium cyanide in 1 liter of water.

A solution suggested for coating piano strings[13] contains about the following:

Copper carbonate	160 grams
Potassium cyanide	320 "
Potassium carbonate	320 "
Boiling water	1 liter

[13] U. S. Pat., 34,640.

The absolute concentration should be such that a good coating of copper is obtained on zinc by dipping a smooth piece of this metal into the solution.

Another solution[14] uses a mixture of the sulphate and acetate, thus:

Copper sulphate	100 grams
Copper acetate	200 "
Potassium cyanide	150 "
Potassium carbonate	150 "
Water	1 liter

Watt's[15] solution is the following:

230 grams copper sulphate in 1 liter water.
Ammonium hydroxide (sp. gr. 0.88) until precipitate formed just dissolves.
1 liter water.

To this solution is added a strong solution of potassium cyanide until the blue color of the ammoniacal copper is discharged. This requires about 600 grams of potassium cyanide in 2 liters of water.

This solution may be used hot or cold, but preferably at 50° to 55° C. This is used for coating zinc and iron.

A dilute solution has been suggested by Depierre[16] for plating zinc. This consists of:

Copper acetate	14 grams
Potassium cyanide (95 percent)	20 "
Ammonium hydroxide (sp. gr. 0.88)	8 "
Water	1 liter

Roseleur's solution[17] for zinc and iron is:

Solution 1:

Sodium bisulphite	16 grams
Sodium carbonate	40 "
Water	1 liter

This is mixed with:

Solution 2:

Copper acetate	40 grams
Ammonium hydroxide (sp. gr. 0.88)	14 "

[14] U. S. Pat., 129,124.

[15] Watt and Philipp: p. 155; Fontaine: p. 133; McMillan: p. 145.

[16] McMillan: p. 145.

[17] Fontaine: p. 133; Langbein: p. 303; Brannt: p. 226; Watt and Philipp: p. 156; McMillan: p. 145. Electrochemist and Met., 3, 254 (1903).

To this mixture is added:

Solution 3:

Potassium cyanide (70 percent)	56 grams
Water	1 liter

The bisulphite acts as a brightener. This solution works best hot. For cold work a solution[18] containing about three times as much sodium bisulphite, twice as much sodium carbonate and about 25 percent less cyanide than the above. It is claimed, however, that the excess of sodium salts are sometimes detrimental rather than helpful. The use also of separate baths for cold and hot copper plating, except for obtaining particular tones, is questioned.[19] A number of these solutions have been suggested by Roseleur, but, since they are practically obtained by changing slightly the concentration of one or another of the ingredients, only one[20] solution will be given. This is to be used warm:

Copper acetate	20 grams
Potassium cyanide	22 "
Sodium sulphite	8 "
Ammonium hydroxide (0.88)	12 "
Sodium carbonate	20 "
Water	1 liter

It is claimed[21] that the solutions given by the text books are useless, since they contain an excess of ammonia or other alkali. They are also too strong. The following solution is recommended instead:

Solution 1:

Copper sulphate	36 grams
Ammonium hydroxide	26 c.c.
Water	182 c.c.

Solution 2:

Potassium cyanide	38 grams
Water	148 c.c.

These are mixed and made up to 1 liter, and worked with a current density of 0.4 to 0.5 ampere per sq. dm.

The following is recommended highly by Langbein:[22]

Sodium carbonate...	250 grams dissolved in
Water	7 liters, to which solution is added
Sodium bisulphite...	200 grams, and
Copper acetate.....	200 grams

[18] Langbein: p. 303.
[19] Langbein: p. 304.
[20] McMillan: p. 145.
[21] Cowper-Coles: Electrochemist and Met., 3, 257 (1903).
[22] P. 304.

This solution is mixed in the cold with

Potassium cyanide (98 percent)	225 grams
Water	3 liters

It is claimed that the current does not have to be high in this solution, being about 0.4 ampere per sq. dm. This may be used on practically all metals, zinc included.

The solution actually used in practice contains:

Copper carbonate	38-50 grams
Potassium cyanide	75-100 "
Potassium carbonate	15-30 "
Sodium bisulphite	15-25 "
Water	1 liter

Stockmeier recommended[23] the substitution of the neutral sulphite in the above formula, with minor changes in concentration.

Copper acetate may be replaced by the carbonate, which in turn may be prepared from the sulphate by precipitation with sodium carbonate solution. It is claimed that removal of the sodium sulphate by decantation is beneficial.

Cuprous oxide may also be used as in the following:[24]

Sodium bisulphite	300 grams
Potassium cyanide (98 percent)	300 "
Cuprous oxide	100 "
Water	15 liters

This is used with 0.3 ampere per sq. dm., at a voltage of 2.5 to 3.0 volts. This solution is used in practice.

Cuproso-cupric sulphite which contains enough sulphurous acid to reduce the cupric copper present may be advantageously used. These formulæ will not be given, for they give practically the same solution in the end. This salt is recommended on account of its cheapness and from the fact that no cyanogen is liberated when the solution is made up.

Pfanhauser[25] recommends the following bath:

Sodium sulphate anhyd	200 grams
Sodium acid sulphite	200 "
Copper potassium cyanide	300 "
Ammonia-soda	100 "
Potassium cyanide	10 "
Water	10 liters

[23] Langbein: p. 305.

[24] Langbein: p. 306.

[25] Elektroplattierung, *l. c.;* Langbein: p. 307.

A formula similar to this, but containing sodium carbonate instead of sulphate, was claimed by Pfanhauser[26] to give excellent deposits. This was modified by Fischer,[27] who attempted to prepare the solution by adding sodium sulphite instead of the acid salt with the carbonate, which he assumed reacted, thus:

$$2NaHSO_3 + Na_2CO_3 = 2Na_2SO_3 + CO_2 + H_2O$$

He obtained a bad deposit. Upon investigation of Pfanhauser's solution it was found to contain some acid sulphite, which enhances the character of the deposit. In other words, the above reaction does not run to completion. Sulphuric acid was also shown to have a beneficial action upon the deposited copper. By adding some acid sulphite, therefore, he obtained a good deposit. The solution was:

Sodium sulphite, anhyd	20 grams
Sodium bisulphite	6 "
Sodium sulphate	20 "
Copper potassium cyanide	30 "
Potassium cyanide	2 "
Water	1 liter

The current density was 0.3 to 0.4 ampere per sq. dm.

Walenn's solution[28] consists of copper cyanide dissolved in a solution of equal parts of potassium cyanide and ammonium tartrate. The exact concentrations are not at hand. Copper oxide and ammoniacal copper solutions are added in making this solution until no hydrogen is evolved at the cathode. The deposit is good, the voltage drop relatively low, the cyanide in the solution hastens or aids the solution of the copper, while the tartrate prevents the formation of a precipitate in the bath.

A dilute solution used for plating cylinders is given by Schlumburger,[29] as follows:

Solution 1:	Parts by Wt.
Potassium cyanide	3
Water	12
Solution 2:	
Copper sulphate	1
Sodium sulphate	2
Sodium carbonate	4
Water	16

[26] U. S. Pat., 976,454.

[27] Elektrochem. Zeit., 8, 192 (1901); Zeit. Elektrochemie, 8, 270 (1902).

[28] Fontaine: p. 142; Watt and Philipp: p. 157.

[29] Fontaine: p. 144.

These are then mixed, and the article coated in the resulting mixture. The plate is thickened up in a stronger solution, differing from the above by containing three parts of ammonium hydroxide and two parts of copper acetate instead of one part of copper sulphate.

A solution[30] for plating copper on the backs of silver mirrors has this composition:

Copper sulphate	100 grams
Ammonium hydrosulphate	5 "
Potassium cyanide	5 "
Water	480 c.c.

This is said to give a brilliant deposit.

The following may be used:[31]

Potassium tartrate	450 grams
Ammonium sulphate	250 "
Copper cyanide	15 "
Water	2.8 liters

This is used hot, and gives a good deposit.

Another bath[32] uses ammonium cyanide and copper oxide rather than the above. It is claimed that the concentration changes on electrolysis are less with this solution than with others, and consequently the deposit is better.

Another solution[33] consisting of

Copper acetate	16 grams
Sodium thiosulphate	12 "
Ammonia	8 "
Potassium cyanide	20 "
Water	1 liter,

is said to give an excellent deposit. The thiosulphate probably acts as a reducing agent.

A solution used in practice is the following:

Cuprous oxide	15 grams
Potassium cyanide	45 "
Sodium thiosulphate	15 "
Water	1 liter

These solutions, as well as those to follow, have a very low concentration of copper ions. Most of the copper exists as part

[30] U. S. Pat., 242,338.
[31] U. S. Pat., 427,513.
[32] U. S. Pat., 557,816.
[33] U. S. Pat., 64,135.

of a complex ion. Since copper dissolves readily in these solutions it follows that the potential between the electrode and solution is high since the ion concentration is low. If this concentration is increased the voltage is decreased. As the amount of free cyanide is increased the ionization of copper is decreased and the voltage difference is increased. As the temperature is increased the metal deposits more easily, however, since the ion concentration increases. The solutions therefore for cold work have less cyanide relative to copper than those for hot work. A solution containing a relatively large concentration of cyanide may be used hot, but requires a high voltage and hence cannot be used advantageously for cold work.

Alkaline baths which do not contain cyanide may next be studied. Elsner's[34] solution contains:

Potassium bitartrate	1 part
Water	10 parts

This solution is saturated with copper carbonate freshly precipitated. The resulting solution is then made more alkaline by adding a small amount of potassium carbonate.

Weil's solution[35] contains:

Copper sulphate	30 grams
Sodium hydroxide (60 percent.)	80 "
Sodium potassium tartrate	150 "
Water	1 liter

For the deposition of copper on iron the modification given below has been tried:[36]

Copper sulphate	60 grams
Sodium hydroxide	50 "
Sodium potassium tartrate	159 "
Water	1 liter

It is claimed that this solution allows a larger range of current density, 0.1 to 0.5 ampere per sq. dm., and gives an excellent adherent deposit of copper. The voltage is lower than for the cyanide bath, and 100 percent efficiency is obtained at both electrodes.

[34] McMillan: p. 145; Watt and Philipp: p. 156; Electrochemist and Met., 3, 256 (1903).

[35] Langbein: p. 309; Brannt: p. 230; Watt and Philipp: p. 158; McMillan: p. 145. See also U. S. Pat., 33,721.

[36] Brown and Mathers: Jour. Phys. Chem., 10, 19 (1906).

Another solution[37] recommended by Roseleur is the following:

Copper sulphate	19 grams
Acid potassium tartrate (lime free)	19 "
Sodium carbonate	42.5 "
Sodium hydroxide solution (sp. gr. 1.12)	75 c.c.
Water	1 liter

Gulensohn's solution[38] consists of freshly precipitated copper phosphate dissolved in a solution of sodium hydroxide. Ammonium hydroxide may be added to aid solution and to render the deposit brighter and denser.

The following solution[39] has been patented by Kern:

Copper fluosilicate	12 parts
Ammonium fluosilicate	8 "
Ammonium tartrate	6 "
Ammonium fluoride	5 "
Water	100 "

This solution should be kept alkaline or neutral with ammonium hydroxide.

"Addition Agents."

A classic case of an addition agent, and the case studied[40] first, is that of gelatine. One part of gelatine to one thousand parts of solution gives a very finely crystalline, almost burnished deposit. Glue[41] accomplishes the same result. The deposit is smoother when made at 30° over that at 20° C. When a solution of about 6.5 percent copper fluosilicate with about 3.5 percent hydrofluosilic acid is used the deposit is better when one part of gelatine[42] to five thousand of solution is present. The temperature effect here is the same as in the sulphate solution.

It has been noticed[43] that tin salts in a copper sulphate electrolyte improved the character of the deposited metal. It is stated that the drop of potential at the electrode is decreased by the presence of a small amount of tin salt.

An extract of oak-wood,[44] which consists chiefly of tannic

[37] Langbein: p. 309.

[38] Watt and Philipp: p. 157; Electrochemist and Met., 3, 256 (1903).

[39] U. S. Pat., 946,903.

[40] Von Hübl: Mitteilungen des k. u. k. Militär-Geographischen Instituts, **6**, 51 (1886); Mueller and Bahntje: Zeit. Elektrochemie, **12**, 317 (1906).

[41] Trans. Am. Electrochem. Soc., **6**, 33 (1904).

[42] Kern: Trans. Am. Electrochem. Soc., **15**, 455 (1909).

[43] Kiliani: Berg. und Huttenmannisches Zeitung (1885) p. 249; Kern: Trans. Am. Electrochem. Soc., **15**, 441 (1909); Wen and Kern: *Ibid*, **20**, 121 (1911).

[44] Trans. Am. Electrochem. Soc., **8**, 83 (1905).

acid, is said to produce a smoother deposit of copper from the sulphate solution.

In the case of a sodium chloride solution of cuprous chloride[45] (about 2 percent cuprous chloride and 15 percent sodium chloride) neither gelatine nor dextrine, in proportions up to one part per five hundred of solution, prevented the formation of large crystals.

A solution with an addition agent has been patented.[46] It contains:

Copper fluosilicate	12 parts
Ammonium fluosilicate	8 "
Ammonium fluoride	5 "

The bath may be kept acid with fluosilicic acid, in which case there is added:

Gelatine or tannin	0.06 part

The solution may also be maintained neutral with aluminum fluosilicate, in which case aluminum hydroxide[47] probably acts as addition agent.

Another patented solution[48] contains:

Copper sulphate	200 grams
Sulphuric acid	15 "
Alum	15 "
Water	1 liter

In all of the cases considered so far the agents are colloids. Gelatine, glue, tannic acid, stannic acid and hydrated aluminum oxide[49] from the aluminum alum are all capable of forming colloidal solutions or suspensions. These colloids under the influence of electrical stress in acid solutions migrate toward the cathode. At the cathode the metal is caused to deposit in a denser, harder and brighter form. Dense, smooth metal is obtained by working it cold, which process gives smaller crystals. A bright finish is obtained over a metal by burnishing, or, in other words, by working until practically a surface is obtained

[45] Kern: *l. c.*, p. 455.
[46] U. S. Pat., 946,903.
[47] Bancroft: Trans. Electrochem. Soc., **21**, 236 (1912).
[48] U. S. Pat., 976,455.
[49] Bancroft: *l. c.*

which consists of the so-called amorphous metal. Light is reflected because the very fine-grained particles, being so small, lie so close together that practically a continuous coating is obtained. Hard copper is obtained by working also; this, therefore, must be due to small crystals. A decrease in the size of the crystals of copper deposited in the presence of addition agents is sufficient, therefore, to explain the beneficial effect due to these reagents. Given, therefore, the colloid with a tendency to go to the cathode, how does it decrease the crystal size of the deposited copper or metal in general? Copper is not deposited directly on the cathode in the crystalline form. The intermediate state may be considered as analogous to a "melt."[50] Or it may be assumed, instead, that the solution holds the metal in colloidal suspension[51] during the passage from the ionic to the crystalline state. With either assumption the colloidal addition agent would act as a protective colloid to the metal. As more metal is reduced the concentration reaches a point where metal must deposit. Since it deposits in intimate contact with the protective agent it does not form large crystals, but is brought down in some cases very finely crystalline indeed. This state gives rise to the enhanced character of the deposit.

Aside from any assumptions, however, it is known that the presence, as well as the increase in the concentration, of gelatine in solution decreases the size of the crystals of salts[52] crystallizing from that solution. The case of electrolytic deposition is analogous. There must be a decrease in the crystal size due to the presence of the colloid in electrolysis.

From what has been said the conclusion is that the colloid is deposited along with the metal, probably as a protective film over the surface of the crystals. This follows from the fact that copper deposited from solutions containing a large amount of gelatine is very brittle,[53] the brittleness decreasing as the gelatine is decreased. Here the film becomes thinner and exerts relatively less influence.

[50] Bennett: *l. c.*, p. 256.
[51] Spear: Eighth Int. Cong. App. Chem., **21**, 99 (1912).
[52] Hatschek: Zeit. Kolloide Chem., **8**, 196 (1911).
[53] Bennett: *l. c.*, p. 264.

The fact that gelatine does not prevent the formation of large crystals during the electrolysis of a sodium chloride solution of cuprous chloride merely means that the tendency for the gelatine to move to the cathode in this solution is negligible.[54] Since this agent is not carried to the cathode it obviously cannot affect the conditions there. It is practically certain that the beneficial action would be apparent in a hydrochloric acid solution of cuprous chloride.

Another class of addition agents are strong reducing agents. The deposition of copper from fluosilicate solutions takes place, giving a denser, smoother deposit in the presence of pyrogallol.[55]

A commercial bath is as follows:

Copper sulphate	175 grams
Sulphuric acid	45 "
Water	1 liter
Molasses 1 cup per 10 gallons	60 c.c. per 10 liters of solution

It is claimed[56] that the deposit is excellent in this solution for a time, but that it goes bad later. Some condition, of course, changes. It has never been determined whether or not the disturbing factor is a decomposition product of the addition agent. The bath, at any rate, is used commercially.

Benzoic acid is said to cause the deposition of a tough and bright deposit.[57]

Hydroxylamine[58] in a solution is said to give a more coherent deposit of the metal than otherwise.

Sugar[59] added to a solution is also said to give a beneficial action.

Since sugar makes some suspensions[60] more stable there is unquestionably some absorption present. This may explain the action of this as well as some of the other reducing agents in so far as they decrease the crystal size.

[54] Mueller and Bahntje: *l. c.*

[55] Kern: *l. c.*, p. 469.

[56] Emrich: Trans. Am. Electrochem. Soc., **15**, 476 (1909).

[57] Metal Ind. (1903), p. 79.

[58] Trans. Am. Electrochem. Soc., **6**, 29 (1904).

[59] Dede: Zeit. Elektrochemie, **17**, 238 (1911).

[60] Zsigmondy: Colloids and the Ultra-Microscope. Translated by Alexander, p. 43 and 86 (1909).

An important case of addition is that of alcohol in the coulometer solution.[61] This consists of:

Copper sulphate	150 grams
Sulphuric acid	50 "
Alcohol	50 "
Water	1 liter

The explanation of the better deposit obtained here is probably due to the fact that alcohol practically prevents the formation of cuprous oxide by forcing the concentration of cuprous ion to a low value.[62] It has been shown that the presence of cuprous oxide tends to make the deposit uneven.[63] The alcohol, by preventing the formation of the objectionable product, may give a better metal.

The action of the straight reducing agents is not so clear. It is probable, however, that the smoothness and adherence of the deposit is due to purity, that is, freedom from oxide, occasioned by the reducing action of the reducing agent. There is no reason for any tendency to decrease the crystal size.

The inorganic addition agents, such as potassium nitrate, nitric acid and sodium chlorate, act because their resulting solutions tend to dissolve the copper and copper oxide more than the solution without these substances. This gives rise to a higher voltage between cathode and solution, and hence finer crystals.

The addition of a 0.7 percent of zinc sulphate to a 10 percent copper sulphate and 10 percent sulphuric acid solution is said[64] to prevent the deposition of copper in botryoidal form.

The addition of a small amount of sodium chloride to a solution of copper sulphate is said[65] to improve the character of the deposited copper. No satisfactory evidence exists, however, to support this statement. There seems to be no reason why a small amount of sodium chloride, added to a solution with electrolytic copper anodes, should affect in any marked degree the deposit formed from this solution.

For the sake of reference the solutions given above and the "addition agents" are grouped in Tables III, IV and V.

[61] Oettel: Chem. Zeitung, **17**, 543 and 547.
[62] Foerster and Seidel: Zeit. für anorg. Chem., **14**, 135 (1897).
[63] Zeit. Elektrochemie, **3**, 482 (1897).
[64] Phil. Mag., [4], **1**, 42 (1871).
[65] Wen and Kern: *l. c.*, p. 170.

Table IV.

Alkaline Copper Plating Solutions.

Special Use	Parts by Weight of Ingredients																									
	Copper Carb.	Copper Sulp.	Copper Acetate	Cuprous Oxide	Copper Pot. Cyanide	Copper Cyanide	Copper Fluosilicate	Potassium Cyanide	Potassium Carbonate	Am. Hydro. Sp. Gr. 0.88	Sodium Bisulphite	Sodium Carbonate	Sodium Sulphite	Sodium Sulphate	Ammonia Soda	Am. Hydro-Sulphate	Ammonium Sulphate	Potassium Tartrate	Sodium Thiosulphate	Potassium Bi-Tartrate	Sodium Hydroxide	Rochelle Salts	Ammonium Fluosilicate	Ammonium Tartrate	Ammonium Fluoride	Water
	60	. .	. .	. .	. .	. .	. .	80	. . .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	.	. .	. .	. .	. .	. .	1000
Wire	160	. .	. .	. .	. .	. .	. .	320	320	. . .	. .	. .	. .	. .	. .	.	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
		100	200	. .	. .	. .	. .	150	150	. . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
Zinc	. . .	60	. .	. .	. .	. .	. .	150	. . .	q.s.	.	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
Zinc	. . .	. .	14	. .	. .	. .	. .	20	. . .	8	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
Zinc and Iron .	. . .	. .	20	. .	.	. .	. .	28	. . .	7	8	20	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
			20	. .	. .	. .	. .	22	. . .	12	. .	20	8	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
		36	. .	. .	. .	. .	. .	38	. . .	26	.	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
All Metals . .	. . .	. .	20	. .	. .	. .	.	22	. . .	. . .	20	25	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
	45	. .	. .	. .	. .	. .	. .	85	23	. . .	20	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
				7	. .	. .	. .	20	. . .	. . .	20	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
					30	. .	. .	1	. . .	. . .	20	. .	. .	20	10	. .	. .	. .	. .	. .	. .	.	. .	. .	. .	1000
					30	. .	. .	2	. . .	. . .	6	. .	20	20	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
Cylinders . . .	. . .	36	. .	. .	. .	. .	. .	108	. . .	. . .	. .	144	. .	72	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
Silver	. . .	200	. .	. .	. .	. .	. .	10	. . .	. . .	. .	. .	. .	. .	. .	10	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
						5	. .	. .	. . .	. . .	. .	. .	. .	. .	. .	. .	85	150	. .	. .	. .	. .	. .	. .	. .	1000
			16	. .	. .	. .	. .	20	. . .	8	. .	. .	. .	. .	. .	. .	. .	. .	12	. .	. .	. .	. .	. .	. .	1000
				15	. .	. .	. .	45	. . .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	15	. .	. .	. .	. .	. .	. .	1000
	q.s.	. .	. .	. .	. .	. .	. .	.	q.s.	. . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	100	. .	. .	. .	. .	. .	1000
		30	. .	. .	. .	. .	. .	. .	. . .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	50	150	. .	. .	. .	1000
Iron	. . .	60	. .	. .	.	. .	. .	. .	. . .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	50	159	. .	. .	. .	1000
		19	.	. .	. .	. .	. .	.	. . .	. . .	. .	43	. .	. .	. .	. .	. .	. .	. .	19	8	. .	. .	. .	. .	1000
							120	. .	. .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	. .	80	60	50	1000

Table III.

Acid Copper Plating Solutions.

(q. s. = sufficient quantity.)

Special Use	Parts by Weight of Ingredients												Remarks
	Copper Sulphate	Copper Oxalate	Copper Nitrate	Copper Acetate	Copper Am. Sulphate	Sulphuric Acid	Nitric Acid	Acetic Acid	Oxalic Acid	Ammonium Nitrate	Ammonium Oxalate	Water	
Electro-typing .	150	. . .	. . .	. .	. .	. .	. .	. . .	. . .	. . .	. . .	1000	
Plating. .	150	. . .	. . .	. .	. .	100	. . .	. . .	. . .	. . .	. . .	1000	
Galvano-plasty. .	200	. . .	. . .	. .	. .	20	. . .	. .	. . .	. . .	. . .	1000	
										25–60	. . . . .	1000	Form electro-lytically
		q.s.	. . .	. .	. .	. . .	. . .	. . .	Ex-cess	. . .	q. s.	1000	
			350	. .	. .	. . .	Ex-cess	. . .	. . .	. . .	. . .	1000	
				5	. .	. . .	. . .	Ex-cess	. .	. . .	. . .	1000	
					40	Ex-cess	. . .	. .	. . .	. .	.	1000	

Table V.

Addition Agents Beneficial in Copper Deposition.

Solution	Colloids	Reducing Agents	Inorganic Agents
Sulphate	Gelatine Glue Tin Salts Tannic Acid Alum	Molasses Benzoic Acid Hydroxyl Amine Sugar Alcohol	Potassium Nitrate Nitric Acid Sodium Chlorate Zinc Sulphate
Fluosilicate	Gelatine Aluminum fluosilicate	Pyrogallol	

Electrochemical Laboratory,
Cornell University.

A paper presented in the Symposium on Electrodeposition of Metals, at the Twenty-Third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913, President W. Lash Miller in the Chair.

THE ELECTRODEPOSITION OF BRASS AND BRONZE

By C. W. Bennett.

The solutions used for the deposition of these alloys are those in which the concentration of copper as ion is low. They are, therefore, solutions of complex salts. The difficulty experienced in the deposition of brass is not so great as that encountered with bronze. In the former case it is only necessary to obtain a solution in which the voltages required to deposit the two metals are as close together as possible. Having obtained this, the current density and relative concentration of the metals in the solution may be varied until the deposit contains both metals in the desired proportions. In the case of bronze, however, another condition is introduced which is practically very hard to regulate. Substitution of tin for zinc introduces the possibility of the oxidation of tin and also of its dissolving and forming a colloid. In this case there is a possibility of the depositing metals existing in the solution in the following forms: cupric, cuprous, stannous and stannic ions and as colloidal oxide. Some of the bronzing solutions give lovely deposits for a short time. After running for a while the deposit becomes rich in either copper or tin. This is due to the fact that some of the changes mentioned above have altered the solution so that the original conditions no longer obtain. The most important changes, it is believed, are the oxidation of the tin over to the stannic condition, and the formation of the colloidal oxide. A plating can be obtained, therefore, if a large volume of the solution be used or if a new solution be continuously run in. No solution, however, gives satisfactory plate continuously. As may be expected, therefore, while brass is plated commercially, no satisfactory solution has ever been suggested for bronze. The solutions recommended for these depositions are given below.

Part I. Brass.

Heeren's[1] solution is the following:

Copper sulphate	3 grams
Zinc sulphate	26 "
Potassium cyanide	60 "
Water	1 liter

Roseleur recommends three solutions.[2] The first is:

Copper carbonate, freshly precipitated	12.0 grams
Zinc carbonate, freshly precipitated	7.0 "
Potassium cyanide	20.0 "
Sodium carbonate	20.0 "
Sodium bisulphite	20.0 "
Arsenious acid	0.2 "
Water	1 liter

For all metals this bath is recommended:

Copper acetate	12.5 grams
Zinc chloride	12.5 "
Sodium carbonate	30.0 "
Sodium bisulphite	20.0 "
Potassium cyanide	35.0 "
Arsenious acid	0.2 "
Water	1 liter

It is stated that these solutions should be boiled before being used. Working for several hours is said to make them work better. The amount of sodium carbonate may be increased to about 90 grams per liter if iron is to be plated.

Lastly, the following is recommended for coating zinc:

Copper acetate	14 grams
Zinc chloride	14 "
Sodium bisulphite	28 "
Potassium cyanide	30 "
Ammonia (sp. gr. 0.9)	16 "
Water	1 liter

Cuproso-cupric sulphite or cuprous oxide may be used in the preparation of the brassing solution. A solution from cuprous oxide will be given:[3]

Cuprous oxide	8.5 grams
Zinc chloride	8.0 "
Potassium cyanide	30.0 "
Sodium bisulphite	20.0 "
Water	1 liter

[1] The references given simply to name and page refer to the books of these authors. Watt and Philipp: p. 381; McMillan: p. 283.

[2] Langbein: p. 324; Brannt: p. 239; McMillan: p. 283; Watt and Philipp: p. 381.

[3] Langbein: p. 326.

Copper and zinc cyanides or potassium cupro- and potassium zinc cyanides may also be used, the final solution being practically the same as those given above.

Gore[4] recommends this solution for iron:

Copper acetate	12.5	grams
Zinc chloride	10.0	"
Potassium cyanide	38.0	"
Sodium carbonate	100.0	"
Sodium bisulphite	20.0	"
Water	1	liter

Morris and Johnson[5] recommend the following:

Copper cyanide	12.5	grams
Zinc cyanide	6.2	"
Potassium cyanide	100.0	"
Ammonium carbonate	100.0	"
Water	1	liter

The concentration of cyanide is so high here that it is doubtful whether deposition will occur, except at a high temperature or with a high current density.

Pfanhauser[6] recommends the following for coating upon all metals:

Copper cyanide	42	grams
Zinc cyanide	42	"
Potassium cyanide	4	"
Ammonium chloride	4	"
Ammonia-soda	20	"
Water	1	liter

Another solution[7] is the following:

Copper chloride	5.0	grams
Zinc sulphate	10.0	"
Potassium cyanide	2.4	"
Potassium carbonate	120.0	"
Ammonium nitrate	61.0	"
Water	1	liter

Several other solutions differing slightly from the above[8] may be given:

Copper chloride	7.5	grams
Zinc sulphate	15.0	"
Potassium carbonate	180.0	"
Ammonium nitrate	90.0	"
Water	1	liter

[4] Langbein: p. 328; Brannt: p. 242.

[5] Brannt: p. 242; McMillan: p. 283; Watt and Philipp: p. 380.

[6] Brannt: *l. c.*, p. 243.

[7] Fontaine: p. 145; McMillan: p. 283; Watt and Philipp: p. 378.

[8] Fontaine: p. 146; McMillan: p. 283; Watt and Philipp: p. —.

Another solution is:

Copper chloride	5.5 grams
Zinc sulphate	8.0 "
Potassium carbonate	65.0 "
Potassium cyanide	10.0 "
Water	1 liter

Russell and Woolrich's solution contains the following:

Copper acetate	150 grams
Zinc acetate	15 "
Potassium acetate	150 "
Potassium cyanide	to dissolve precipitate first formed
Water	1 liter

Walenn recommends the following:

Copper nitrate, Zinc sulphate	Saturated solution
Ammonium hydroxide	Sufficient to redissolve hydroxides
Potassium cyanide	In excess

Salzède's solution is the following:

Copper chloride	3 grams
Zinc sulphate	7 "
Potassium cyanide	10 "
Potassium carbonate	100 "
Water	1 liter

Watt's solution is:

Copper acetate	4.5 grams
Zinc sulphate	9.0 "
Potassium cyanide	7.5 "
Potassium hydroxide	67.0 "
Ammonium hydroxide	30.0 "
Water	1 liter

A patented[9] solution contains:

Copper carbonate (freshly precipitated)	35 grams
Zinc oxide	23 "
Potassium cyanide	165 "
Potassium carbonate	75 "
Water	1 liter

The addition of cupric ammonide ($Cu_2O.4NH_3$)[10] is said to aid the deposition of a good brass plate.

Some commercial brass plating solutions may be given:

Copper carbonate (dry)	50 grams
Zinc sulphate	30 "
Potassium cyanide	75 "
Water	1 liter

Copper anodes are used and zinc salt added from time to time.

[9] U. S. Pat., 34,640.

[10] Phil. Mag. [4], 1, 43 (1871).

Another solution used is the following:

Copper carbonate	50.0 grams
Zinc carbonate	10.0 "
Potassium cyanide	110.0 "
Sodium carbonate	14.0 "
Sodium bisulphite	3.5 "
Ammonium hydroxide	7.0 "
Water	1 liter

Another combination[11] highly recommended is the following:

Solution 1:

Copper sulphate	112 grams
Potassium cyanide	112 "
Sal soda	69 "
Potassium hydroxide	5 "
Water	⅔ liter

Solution 2:

Zinc sulphate	37 grams
Potassium cyanide	35 "
Sal soda	25 "
Potassium carbonate	6 "
Water	⅓ liter

The current is started on solution 1, and, while working slowly, solution 2 is added slowly until the desired brass is obtained.

These solutions are all made up to give a brass containing 30 to 40 percent zinc. Consequently anodes of this composition are used.

A solution used in the laboratory at Cornell contains:

Copper sulphate	25 grams
Zinc sulphate	29 "
Potassium cyanide	to dissolve the precipitate
Water	1 liter

These solutions are tabulated in Table I.

Part II. Bronze.

Bronzing solutions are also numerous. The most striking fact, however, is that practically all of them are impracticable. None that has been tried personally gives a satisfactory plate. Commercially, of course, the bronze color is imitated with brass, or by coloring with some reagent.

[11] National Electroplaters' Assoc., March 29, 1912.

Table I.

Solutions for the Deposition of Brass.

Parts by weight of ingredients to 1000 parts of water

	Copper Sulphate	Copper Carbonate	Copper Acetate	Copper Cyanide	Cuprous Oxide	Copper Chloride	Copper Nitrate	Zinc Sulphate	Zinc Carbonate	Zinc Chloride	Zinc Cyanide	Zinc Acetate	Zinc Oxide	Potassium Cyanide	Sodium Carbonate	Sodium Bisulphite	Arsenious Acid	Ammonium Hydroxide	Ammonium Carbonate	Ammonium Chloride	Ammonia-Soda	Ammonium Nitrate	Potassium Carbonate	Potassium Acetate	Potassium Hydroxide	Sal-Soda	Water
1	3	. . .	. . .	. .	. .	. .	. .	26	. .	. . .	. .	. .	. .	60	. .	. . .	. .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	1000
2	. .	12	. . .	.	. .	. .	. .	. . .	7	. . .	. .	. .	. .	20	20	20	0.2	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
3	. .	. . .	13	. .	.	. .	. .	. . .	. .	13	. .	. .	. .	35	30	20	0.2	. .	. .	. .	. .	. .	. .	. .	. .	. .	1000
4	. .	.	14	. .	. .	. .	. .	. . .	. .	14	.	. .	.	30	. . .	28	. . .	16	. .	. .	. .	. .	. .	. .	. .	. .	1000
5	. .	.	. . .	. .	9	. .	. .	. .	. .	8	. .	. .	. .	30	. . .	20	. . .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	1000
6	. .	. . .	13	.	. .	. .	. .	. . .	. .	10	. .	. .	. .	38	100	20	. . .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	1000
7	. .	. . .	. . .	13	. .	. .	. .	. . .	. .	. . .	7	. .	. .	100	. . .	. . .	. . .	. . .	100	. .	. .	. .	. .	. .	. .	. .	1000
8	. .	. . .	. . .	42	. .	. .	. .	. . .	.	. . .	42	. .	. .	4	. . .	. . .	.	. . .	. .	4	20	. .	. .	. .	. .	. .	1000
9	. .	. . .	. . .	. .	. .	5	. .	10	. .	. . .	. .	.	.	2.4	. . .	. . .	. . .	. . .	. .	. .	. .	61	120	. .	. .	. .	1000
10	. .	. . .	. . .	. .	. .	8	. .	15	. .	. . .	. .	. .	. .	. . . .	. .	. . .	. . .	. . .	. .	. .	. .	90	180	. .	. .	. .	1000
11	. .	. . .	. .	. .	. .	6	. .	8	. .	. .	. .	.	. .	10	. . .	. . .	. . .	. . .	. .	. .	. .	. .	65	. .	. .	. .	1000
12	. .	. . .	150	. .	.	. .	. .	. . .	. .	. . .	. .	15	. .	q. s.	. . .	. . .	. .	. . .	. .	. .	. .	. .	. .	150	. .	. .	1000
13	. .	. . .	. .	. .	. .	. .	s.	s.	. .	. . .	. .	. .	. .	ex	. . .	. . .	. . .	q. s.	. .	. .	. .	. .	. .	.	. .	. .	1000
14	. .	. . .	. .	. .	.	3	. .	7	. .	. . .	. .	. .	. .	10	. . .	. . .	. . .	. . .	. .	.	. .	. .	100	. .	. .	. .	1000
15	. .	.	4.5	. .	. .	. .	. .	9	. .	. . .	. .	. .	. .	7.5	. . .	. . .	. . .	30	. .	. .	. .	. .	.	. .	67	. .	1000
16	.	35	. . .	. .	.	. .	. .	.	. .	. . .	. .	. .	23	165	. . .	. . .	. . .	. . .	. .	. .	. .	. .	75	.	. .	. .	1000
17	. .	50	. . .	. .	. .	. .	. .	30	. .	. . .	. .	. .	. .	75	. . .	. . .	. . .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	1000
18		50	. .	. .	. .	.	. .	. . .	10	. . .	. .	. .	. .	110	14	4	. . .	7	. .	.	. .	. .	. .	. .	. .	. .	1000
19	112	. .	. . .	. .	. .	.	. .	37	.	. .	. .	. .	.	147	. . .	. . .	. . .	. . .	. .	. .	. .	. .	6	. .	5	94	1000
20	25	. . .	. . .	. .	. .	. .		29		.		. .	. .	q. s.		. .	. . .	. . .	. .	. .	. .	. .	. .	. .	. .	. .	1000

A patented solution[12] contains:

Copper carbonate	37.5 grams
Tin oxide	7.5 "
Potassium carbonate	15.0 "
Potassium cyanide	202.5 "
Water	1 liter

Failing to obtain good deposits with any of the solutions recommended by plating handbooks, Langbein recommends[13] the following:

Solution 1:

Sodium pyrophosphate	50 grams
Water	1 liter

To this solution are added the following solutions 2 and 3 in proportions depending on the composition bronze desired:

Solution 2:

Sodium pyrophosphate	Saturated solution
Copper phosphate	To saturation

Solution 3:

Sodium pyrophosphate	Saturated solution
Stannous chloride	To saturation

If the deposit is too light more copper solution is added; if too dark, more tin. The anodes of cast bronze are said to dissolve readily in the solution.

Salzède's[14] solution, to be used at 30° to 35° C., is:

Cuprous chloride	1.5 grams
Stannous chloride	1.2 "
Potassium cyanide	10.0 "
Potassium carbonate	100.0 "
Water	1 liter

Gountier's solution for plating wrought and cast iron is the following:[15]

Potassium ferrocyanide	30 grams
Cuprous chloride	15 "
Stannous chloride	40 "
Sodium thiosulphate	40 "
Water	1 liter

[12] U. S. Pat., 34,640.

[13] Langbein: p. 337; Brannt: p. 248.

[14] Langbein: p. 336; Brannt: p. 247; McMillan: p. 287; Fontaine: p. 146.

[15] Brannt: p. 247.

Roulz's solution[16] contains:

Copper cyanide	5 grams
Tin oxide	2 "
Potassium cyanide	40 "
Water	1 liter

Elsner's solution[17] is the following:

Copper sulphate	70 grams
Stannic chloride	8 "
Potassium hydroxide	Small amount
Water	1 liter

Solutions recommended by Weiss[18] are the following:

Cupric chloride	20 grams
Stannous chloride	10 "
Potassium carbonate	100 "
Potassium cyanide	10 "
Water	1 liter

This gives a more concentrated solution of copper and tin than Salzède's solution. The other solution recommended by Weiss contains:

Copper sulphate	64 grams
Stannic chloride	9 "
Potassium cyanide	128 "
Potassium hydroxide	Small amount
Water	1 liter

Weil's solution[19] follows:

Copper sulphate	35 grams
Sodium stannate	Sufficient to give required bronze
Soda-lime	80 grams
Rochelle salt	150 "
Water	1 liter

A solution recommended by Currie[20] contains:

Copper sulphate	15.0 grams
Stannous oxalate	4.2 "
Ammonium oxalate	55.0 "
Oxalic acid	5.0 "
Water	1 liter

[16] Brannt: p. 247; McMillan: p. 247.
[17] Brannt: p. 247; McMillan: p. 287.
[18] McMillan: p. 287.
[19] McMillan: p. 287.
[20] Jour. Phys. Chem., **10**, 515 (1906).

Table II.

Solutions for Deposition of Bronze.

	Copper Carbonate	Copper Phosphate	Cupric Chloride	Cuprous Chloride	Copper Cyanide	Copper Sulphate	Tin Oxide	Stannous Chloride	Stannic Chloride	Stannous Oxalate	Sodium Stannate	Potassium Carbonate	Potassium Cyanide	Sodium Pyrophosphate	Potassium Ferrocyanide	Sodium Thiosulphate	Potassium Hydroxide	Rochelle Salt	Soda Lime	Ammonium Oxalate	Oxalic Acid	Water
1	37.5	. .	.	. .		.	7.5	. .	.	. .	. .	15	203		.	.	. .	. .	.	.	.	1000
2	. .	q. s.	.	. .	.	.	. .	q. s.	.	. .	. .	. .	. .	50	.	.	. .	. .	.	.	.	1000
3	. .	. .	.	1.5	.	.	. .	1.2	.	. .	. .	100	10	.	.	.	. .	. .	.	.	.	1000
4	. .	. .	.	15	.	.	. .	40	.	. .	. .	. .	. .	.	30	40	. .	. .	.	.	.	1000
5	. .	. .	.	. .	5	.	2	. .	.	. .	. .	. .	40	.	.	.	. .	. .	.	.	.	1000
6	. .	. .	.	. .	.	70	. .	. .	8	. .	. .	. .	. .	.	.	.	q. s.	. .	.	.	.	1000
7	. .	. .	20	. .	.	.	. .	10	.	. .	. .	100	10	.	.	.	. .	.	.	.	.	1000
8	. .	. .	.	. .	.	64	. .	. .	9	. .	. .	. .	128	.	.	.	q. s.	. .	.	.	.	1000
9	. .	. .	.	. .	.	35	. .	. .	.	. .	q. s.	. .	. .	.	.	.	. .	150	80	.	.	1000
10	. .	. .	.	. .	.	15	. .	. .	.	4.2	. .	. .	. .	.	.		. .	. .	.	55	5	1000
11	. .	. .	.	. .	.	22	. .	. .	.	. .	5.5	. .	. .	.	.		5	150	.	.		1000

Another solution[21] which does not give satisfaction is the following:

Copper sulphate	22.0	grams
Sodium stannate	5.5	"
Sodium hydroxide	5.0	"
Rochelle salt	150.0	"
Water	1	liter

These solutions are tabulated in Table II.

[21] Bennett: p. 266.

Electrochemical Laboratory,
Cornell University.

The Discussion following the Symposium on Electrodeposition of Metals, at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 5, 1913, President W. Lash Miller in the Chair.

DISCUSSION ON THE ELECTRODEPOSITION OF METALS

Dr. W. Lash Miller: We are glad to have with us a number of the members of the American Electro-platers' Society, and we shall now have the pleasure of hearing Mr. Charles H. Proctor, of Arlington, N. J., the founder and first president of that society.

Mr. Chas. H. Proctor: Mr. President and Members of the American Electrochemical Society. As one of your individual members and a representative of the American Electro-platers' Society, I can assure you it gives me great pleasure to meet with you in this your first Symposium on electroplating. I believe this will be a red letter day in the history of the electrodeposition of metals, because from this day hence we can rely upon the electrochemist to participate with us in bringing the art to a higher level, and a day when men of theory can join hands with the practical man who has toiled for years and, with dogged indifference to his surroundings, has brought the art of electroplating to its present standard in the commercial world.

It has not been due to his education, because very few of the men who have made a name for themselves, or have through their limited chemical knowledge become the heads of large plating establishments, have received a college or university education, and many of them not even a high school education; but with persistence they have overcome difficulties and have accomplished results which without that persistence could never have been accomplished.

The several papers to be presented at this Symposium dealing with electrodeposition of the various commercial metals, which through the courtesy of Prof. Richards, your honored secretary, were sent to every member of our Society, show that the work of the various committees has been accomplished in a very thorough manner, and I am sure these papers will prove very valuable as works of reference to every electroplater who has had the privilege of receiving them.

In going over hundreds of complex formulæ contained therein it will be somewhat difficult for a novice to decide what formula to adopt for a successful deposit of the metal to be applied to a given surface. It proves from this mass of information that the time is ripe to accept as standard, formulæ that can be relied upon at all times to fill the demands required of them, and to discard the voluminous mass that has proved that they were produced more from a theoretical standpoint rather than to produce commercial results, which are absolutely necessary in these days of competition in commercial products.

In the past thirty years wonderful developments have been accomplished in electroplating, so far as the electrical and mechanical features of the art are concerned, and during that period very little has been brought forth that has proved to be of any great advantage in the chemical composition of the plating bath.

Patents have been granted indiscriminately, and the men who have the supervision of this work in the Patent Office have no conception of the art or of its requirements; all that was possible for them to do was to refer to known formulæ, and any addition to these formulæ, whether in the form of metallic salt or an organic substance, has been passed upon as an improvement or distinct advantage, and the patent has been granted. Ninety percent of such patents have never had any commercial value. They have been laboratory experiments which should never have gone beyond that unless they had been tried out practically on a commercial scale.

With the co-operation of the members of the American Electrochemical Society interested in this branch of work, and the members of the American Electro-platers' Society, much can be accomplished in simplifying the composition of the plating baths and producing a standard commercial formula containing as few ingredients as possible, because in practice the bath that contains the least ingredients has proved must easier to control than baths with a complex composition.

The members of the American Electro-platers' Society appreciate the work that has been accomplished by individual members of your Society in the electrodeposition of metals, and realize that with the co-operation of such members a wonderful advance can be made in the future.

I have no doubt that there are but few of the gentlemen present at this Symposium, outside of the members of the American Electro-platers' Society, who have any conception of the knowledge required at the present time to successfully supervise and produce profitable results from a large plating department. The plater must not only have a certain amount of practical chemical knowledge, but he must also understand the nature of all the common metals, how to prepare the surfaces for successful deposition; this includes the method of polishing in its various stages, to the finished product, the plating of the rare and commercial metals, the production of chemical and pigment colors in decorative, antique and period effects, so that artistic designs in metals produced according to the various periods from Pompeian to the Flemish Renaissance, the Elizabethan period, the schools of Louis XIV, XV, XVI, and the Colonial and Napoleonic periods down to the conglomeration of mixed periods, can be finished and colored true to the periods in vogue or to the fanciful ideas of the modern consumer.

All metals must be protected from atmospheric influence except in one or two instances, so the modern plater in charge must understand the application of these protective coatings and their nature.

In a large manufacturing concern in the East, which produces articles of metal in everyday use as well as period effects in metals, the plater in charge must produce on the average one new finish or copy a finish of some other manufacturer every day of the year. This will give you some idea of what is expected of the modern electroplater.

Now, gentlemen, the successful electroplater of the future should emanate from your universities. He should receive his chemical, electrical and mechanical education there. In fact, when he graduates from your university he should be not only a theoretical but practical electrochemist and electroplater. This will save much controversy in the future as to who is superior in electroplating, the man who had graduated as an electrochemist with laboratory practice only, or the man who has gained his knowledge by practical experience in producing commercial results.

I know of several large concerns where electrochemists are

employed, and indirectly they have supervision of the plating departments. This diversity of opinion creates considerable feeling with the practical man.

The university man makes an effort to prove his value to his employers, and this is accomplished ofttimes to the disadvantage of the practical man in charge of the plating department, which creates a friction and ofttimes distrust. This problem can be readily solved in the future by training young men who anticipate following the art of electrodeposition of metals as a vocation. Let their laboratory and chemical knowledge be supplemented with practical instruction in the deposition of metals upon a commercial scale; have a plating department in charge of the most experienced and practical man you can obtain, and when your graduates go forth from your university they will be equipped with essential knowledge to take charge of a plating establishment and produce commercial results that are essential in this age of competition.

THE SECRETARY then read the following letter from the acting president of the American Electro-platers' Society:

The members wish to express their thanks for advance papers on electroplating that are to be read at your Spring meeting.

We regard this as a very special honor and feel greatly indebted to the American Electrochemical Society. We know of no work that has been done that equals that accomplished by these papers. Their value to the electro-plating industry can never be estimated, and the interest that they will command will do much for the plater himself.

We wish you a very successful meeting and assure you that we feel proud to be recognized by so learned a body of men.

Thanking you for the personal interest that you took in our behalf we beg to remain,

Yours fraternally,

THE NATIONAL ELECTRO-PLATERS ASSOCIATION,
CHAS. A. STIEHLE, *Acting President.*

DR. W. LASH MILLER: We all appreciate these kind words from the acting president of the American Electro-platers' Society, and also the address which we have heard from the founder and first president of that Society. The way we can do the most good in this matter is to take advantage of the good will displayed by these gentlemen in attending our meeting, and to co-operate with them as far as lies within our power.

Mr. Bennett presented the paper on "Electrodeposition of Copper."

Dr. W. Lash Miller: It is for the discussion of these papers that we are gathered here at this meeting, and I hope that our members, and particularly our visitors, will say exactly what they think about any of the receipts or any of the conclusions contained in the papers which are to be presented during the day.

Mr. Lawrence Addicks: The second half of this paper brings out how many different things have been used as "addition agents" in different cases, and the recognition of drug effects in electrolytes has explained many puzzling difficulties. Dr. Weston has told me of how many cases of diseased nickel plating in the early days were due to platers bailing the solutions into barrels while tank leaks were being repaired. The barrels were usually sized with glue, which put evil spirits into the electrolyte.

In the copper refining plant at present under my supervision we have found that a straight acidified copper sulphate electrolyte produces a deposit which soon becomes covered with fine needles, which grow as the deposit thickens, and act as the nuclei for the tree formations which finally limit the life of the cathode. By trial and accident, combined with close observation on the part of those immediately in charge of the electrolysis, it was found that the addition of mineral oil yielded some substance which turned these needles and made compact nodules of them, or, if enough oil were used, suppressed them entirely. At the same time, however, the structure of the deposit deteriorated into what the men call "cocoa matting" or "rotten" copper. The addition of glue corrects this and gives a firm, hard deposit, so that the proper balance of these two agents, oil and glue, gives excellent deposits, and we can work under much more severe conditions than formerly. Glue, on the other hand, has a marked effect on the working voltage, and its excessive use may increase the potential 30 or 40 percent. It is generally admitted that gelatin diminishes the size of the crystal, and apparently we supply electrochemically the power generally applied mechanically in working the metal. Sufficient gelatin will harden the deposit so that it will ring when struck.

Regarding chlorides, I think it is the custom in all the refineries

to add small quantities of salt or hydrochloric acid. We carry 0.004 percent of chlorine in the electrolyte. I confess I don't know why. It may precipitate any silver that succeeds in dissolving, or it may form an oxychloride with antimony, or it may improve the deposit. I have never tried omitting it, as the cost is negligible and its use almost a tradition. Early in my acquaintance with the refining of copper I was told stories by tankhouse foremen of the terrible things that had happened when copper had been deprived of chlorine, and as nurses' tales have an influence in after life, I put salt in the electrolyte just as I do on my beefsteak.

One other point regarding addition agents: It depends a great deal on whether we are (I) refining the metal, (II) electrotyping or plating, or (III) making copper tubes, etc.

In refining we care only for fair smoothness and structure. In electrotypes we want great smoothness and hardness. In tubes, sheets, wire, etc., we want smoothness, but, above all, ductility. These three processes call for radically different treatment.

Dr. W. D. Bancroft: At the St. Louis meeting, held about ten years ago, I outlined a tentative theory of electroplating, but we did not get much discussion, because one man after another said, "Of course, everybody knows cases to which this theory does not apply," but no one gave me any specific instances at that time or since. I am hoping better things from this meeting today, and in order to facilitate discussion, or give a basis for it, I have had printed some cards which give six self-evident truths in regard to electroplating, no one of which will probably be accepted by more than one or two persons, and I do hope we can get a specific discussion, with specific cases, showing wherein these axioms are considered to be wrong, and afterward I will try to show the mistake on the other fellow's part. The axioms are as follows:

AXIOMS OF ELECTROPLATING.

1. Bad deposits are due to excessive admixture of some compound or to excessively large crystals.

2. Excessive admixture of any compound can be eliminated by changing the conditions so that the compound cannot precipitate.

3. Increasing the current density, increasing the potential difference at the cathode, or lowering the temperature, decreases the size of the crystals.

4. The crystal size is decreased when there are present, at the cathode surface, substances which are adsorbed by the deposited metal.

5. If a given solution will give a good deposit at any current density, it will give a good deposit at any higher current density, provided the conditions at the cathode surface are kept constant.

6. Treeing is facilitated by a high potential drop through the solution and by conditions favorable to the formation of large crystals.

Mr. Charles H. Proctor: In connection with Axiom No. 3 we found in actual practice that the lowering of the temperature, especially of the silver solutions, brought about an increase in the size of the crystals. I believe one of our members here at the present time has a sample of a piece of copper plated with silver in a solution at a low temperature.

Mr. Geo. B. Hogaboom: Speaking about these axioms puts me in mind of a little story I heard in Toronto of a policeman who found a horse dead on Cholmondeley Street. He went to the station house to make a report, and tried to write the name of the street, but finally gave it up and asked the sergeant how to spell the name of Cholmondeley Street. The sergeant said he did not know. They thought over it for some time, and at last the policeman put on his hat and coat and moved toward the door as if he was about to go out. The sergeant asked: "Where are you going?" The policeman replied: "I am going to drag that horse into King Street." (Laughter.) That is the way with these axioms; while they are very good, I am afraid that the plater does not understand them. We will have to drag them some place else so that he can understand them.

Mr. Bennett says that he obtained a better deposit from an alkaline solution than from an acid solution. While the texture of the deposit from an alkaline solution may be better than the texture of a deposit from an acid solution, yet for electroplating the acid solution is better. All ormulo gold work has been plated in an acid solution, as the finish could not be put on over

a cyanide deposit. The lead or the spelter has first been given a coating of cyanide copper, and has then been finished in the acid copper solution. Wherever heavy deposits are required they are put in the acid bath. We have a gentleman with us from Philadelphia who deposits copper an inch and an inch and a half in thickness with the acid copper solution, and it would be impossible for him under any consideration whatever to obtain these deposits from a cyanide solution. If you gold plate over a cyanide copper deposit, you do not get the color, you do not get the wearing qualities, as you would if the acid copper solution were used.

On page 237 Mr. Bennett says: "Copper plating is widely used as a basis for nickel plating on iron, steel and such metals. The object here is to obtain a thin, smooth coating over the surface of the metal of such a nature that the iron will not be dissolved by and contaminate the nickel solution." I respectfully call Mr. Bennett's attention to the fact that all nickel anodes contain anywhere from 4 to 10 percent of iron, and that iron in a nickel solution is very, very common, exceedingly common; and as for iron work contaminating the nickel bath, from an electroplater's standpoint that is not a fact. I have had considerable experience in nickel plating tool work. One of the hardest things to nickel plate, I believe, is a hammer head, and I did several thousand of them. The makers insisted on these being copper plated before nickeling, not to prevent the solution from becoming contaminated with iron and steel—they did not care anything about the solution—but because they thought that would prevent them from rusting. This is the only theory I ever heard put forth to justify a preliminary electroplating with cyanide copper. I do not, however, believe in that theory, because when we did the hammer work we found if the copper deposit was not clear and perfect that after nickel plating the deposit would peel. So we stopped it, and plated directly upon the steel, with nickel, and seldom had a piece to strip.

Our solutions had been running for about eighteen years, without removing the iron, or doing anything to it but adding nickel salts from time to time. It do not know how large a percentage of iron was in the solution; the iron did not affect the deposit. After we stopped the preliminary copper plating

we never had a complaint of a hammer head, and you know what severe usage a hammer receives.

Another thing is that copper in a nickel solution will do a great deal more harm than iron in a nickel solution. If you had a small percentage of copper in the nickel solution you would get "black nickel." I call it "black nickel," but I think Dr. Watts says he does not think it is black nickel; he will not say definitely until he makes an analysis and discovers exactly what it is. Whatever the deposit may prove to be, if you take a double nickel sulphate solution and add to it bisulphite of sodium and sulpho-cyanide of potassium, and no other metal, you get a very heavy black plate which will stand buffing. The work can be and is run for three hours; this deposit is used on automobile parts and on typewriter parts, and is called "black nickel." The voltage to use on such work is 0.5, but if it is increased to 1 volt, black and white streaks will appear, so it would seem it must be some form of nickel.

Still another point: You gentlemen who have experimented in these matters, and you gentlemen who have prepared these papers, have worked with chemically pure chemicals, C. P. chemicals, to a great extent. If a plater gets C. P. chemicals, he is one of the most fortunate of platers. I never saw a plater who always could get C. P. chemicals. I have seen platers discharged because they insisted upon having distilled water. Just as soon as you go into a body of platers and say, "I have to have C. P. this, or C. P. that, or C. P. the other thing, or I cannot get any deposit," every fellow says, "That fellow does not know how to plate; he is only trying to find an excuse."

In regard to these addition agents which are added, we have had some interesting discussions in the meetings of the American Electro-platers' Society over these points. We found with these, and with all the chemicals that were used, that results were not nearly as good as they should have been, theoretically. One of our members was employed at a large plant, and they were adding dextrine to the acid copper solution, thinking they would get a good deposit, and they had all kinds of trouble, and could not make out what was the matter. Upon analysis the dextrine was found to contain 55 percent glue—that is what the electroplater is going up against all the time.

The addition agent that was found to give the most satisfactory results is common alum. Sulphate of alumina, I believe, was added by Cowper-Coles; he patented it, I believe. Mr. Proctor made some experiments with that, but because the solution is patented (and the plater cannot use any solution that is patented) he added common alum, and it gave very good results; no matter how much you added to the solution, a good, smooth deposit was obtained.

Mr. F. A. Lidbury: I was very much interested in Mr. Hogaboom's illustration pleading for a terminological ground upon which we can all meet in common. I would suggest, however, that the ground ought to be chosen in a mutual manner, and he would assist such a choice if he would send his policeman to drag into King Street the ounces per gallon and the degrees Baumé.

Mr. Geo. B. Hogaboom: It seems to me, as representing the platers, that Barclay and Hainsworth in their work on electroplating have taken the proper course by placing alongside of grams and liters the ounces and gallons. Some of these things published upon electroplating, some of these papers, are entirely incomprehensible to the plater. They do not understand them.

I might say, in answer to Mr. Lidbury, some of these papers state that the current density must be so many amperes per square decimeter, and that the anode and cathode must be just so far apart, and that the cathode density and anode density should be different; and in these very illuminating axioms which have been circulated we have statements regarding the potential. For example: "Treeing is facilitated by a high potential drop through the solution and by conditions favorable to the formation of large crystals." If you asked an ordinary plater what potential drop meant he would not know what you were talking about.

To bring the matter back to the practical conditions under which the plater has to work: We will take a nickel solution, say, of 1,500 or 1,800 gallons. In that solution you will require somewhere around 2,000 pounds of nickel anodes, large-sized nickel anodes. There are generally three anode rods and two cathode rods. The connections on the tank are placed permanently. Imagine the job a fellow would have to move the anode in a solution like that, to get it equal to the cathode surface.

Imagine the job a fellow would have so that he would get exactly the proper distance between the anode and cathode. We will suppose that a man was plating chandeliers or electroliers. They have the base and the column and the little caps. The base may have a height of eight inches, and the column an inch and a half in diameter; they all have to be plated in the same bath. How can you regulate the distance between the anode and cathode in that case? If any of you gentlemen went into a job plating shop you would find that they would have fifty jobs in one tank, consisting of bicycle parts, parts of sewing machines, and innumerable other things; and how would you regulate the distance between the anode and cathode in cases like that? The bath is there—a very large bath—and you cannot plate only the small parts or the large parts; you must fill the bath up with the work on hand.

As to the square decimeters, if cathode surface should have so many square decimeters, etc., I would like one of the gentlemen present to compute how many square decimeters there are on a gross of table forks. This is talking from a practical point of view; I cannot tell you anything theoretically, but what the actual conditions are in the metal plating business.

Now, about measuring—take the work I am employed in, deposit work. We have a whiskey bottle—most of you are familiar with that—and we decorate it. We will run through four dozen whiskey bottles, and in that four dozen bottles there will be probably five different designs. Each one of these must have a certain thickness of deposit so that it can be engraved. Probably there are only four or five that will require the same weight of deposit. In the case of a "bar" bottle, where a cheaper grade of work is required, that is, just a few lines here and there, not over 12 pennyweight of silver will be put on the bottle—manufacturers don't figure in grams—while in the same tank there may be another bottle that is to be covered over entirely, and that will require six ounces of silver. We have to put these in side by side, the whole 36 or 48 bottles into one tank, and they come out all exactly at the same time and with the correct weight of silver deposited. This may give some idea of the conditions a plater is up against.

Mr. Lawrence Addicks: I want to voice of word of protest about the use of pure salts. I find the pure food laws under which they must be shipped are very stringent, and it is almost impossible to produce them. I was interested by the reference to one solution which was said to have lasted eighteen years. No one knows how many times new anodes were added to the solution in the eighteen years. The bath should be cleansed periodically and not allowed to become foul, and then the blame for unsatisfactory work would not be laid at the door of relatively pure salts.

Prof. Jos. W. Richards: I suggest that in that solution which lasted eighteen years the impurities were being continuously deposited, the iron continuously deposited with the nickel.

Mr. Geo. B. Hogaboom: I carried on an experiment a short time ago. I sent out 40 pieces of aluminum to as many platers all over the country, and had them deposited with nickel, and had them state the age of all these different solutions, and we just roughly tried to find out how much iron was in each of the deposits, and it was found that the older the solutions the larger the percentage of iron there was in the deposits.

Dr. Edw. F. Kern: As to that electrolyte which has been in constant use for eighteen years, I believe that new chemicals were added to it from time to time, so that the solution would not be so impure as the electroplater might think. When the articles which had been plated were removed from the bath a certain amount of the electrolyte adhered to them, which was washed off and the washings thrown away. The electroplater is continually measuring the strength of his solutions by the use of an hydrometer, determining its concentration in degrees Baumé. In order to maintain his bath at a proper working strength he adds water to bring up the volume, and salts in such amounts that the concentration of the solution is brought to the proper degrees Baumé. This is what may have gone on during the eighteen years referred to, so that in this way the electrolyte was really maintained at a certain commercial purity during that time. The fact is, the electroplater is continually holding his electrolyte to a certain standard of purity by the use of the hydrometer, whereas the electrochemist maintains his electrolyte at a certain

percentage composition and depends upon chemical analyses as his guide.

Mr. Lawrence Addicks: All I am pleading for is fair play. Let the men who furnish the salts supply their share of the impurities as well as the city water works and the man who furnishes the anodes. I do not want any more.

Mr. P. S. Brown: I take the same attitude that the previous speaker took in this matter.

In plating iron, prior to nickel plating, it is quite customary and has been quite customary to plate with copper. Some firms have gone so far as to deposit the copper very heavily. They use a strong cyanide solution, and put on a heavy coating of copper, and then acid copper. I think that history will show that the reason why the copper plating is done prior to the nickel plating is almost always because of the cleansing effect of these solutions. The average copper solution, if it has been in use for some time, contains a very large percentage of carbonate of soda, and also a large percentage of cyanide of potassium. The effect of this alkaline solution, even when cold, is a cleansing one. When you bear in mind that in some plants they use these solutions warm, you will find that the cleansing effect is appreciable. The average plant which strikes up in a copper solution merely strikes the poor and thin deposits of nickel. I have made tests, and never found there was any advantage in the copper weight by weight; in other words, if you can get 5 grams of copper per square inch, and add to it 10 grams of nickel, you have the equivalent of 10 grams of copper and 5 of nickel, or of 15 grams of nickel alone, on actual corrosion tests, in the air, in salt water, and acid water. The whole value of the process of copper plating before nickel plating is in the additional cleansing action and therefore better adherence and better deposits.

Mr. C. W. Bennett: At what voltage does Mr. Hogaboom run his baths?

Mr. Geo. B. Hogaboom: One volt.

Mr. C. W. Bennett: You run it at one volt under all conditions, practically?

Mr. Geo. B. Hogaboom: Practically one volt.

Mr. C. W. Bennett: As I pointed out last year before this Society, there are a number of factors interrelated which control the size of the crystals of a deposited metal. First, the rotation of the cathode is equivalent to cold-working the metal; second, working at high temperatures is equivalent to annealing the metal, that is, causes the crystals to grow larger than if the metal was deposited at a lower temperature; lastly, current density or rate of precipitation is a very important factor. With a high current density, and therefore a rapid rate of deposition, the metal is always obtained in a finer crystalline state because the rate of crystallization is very rapid. Conversely, with a low current density the crystals are large because the rate of crystallization is slow.

The electroplater controls the progress of his process by controlling the voltage. Let us inquire what will happen in a cyanide solution during electrolysis with constant voltage at different temperatures. The conductance of the solution decreases with a decrease in temperature, so that at a constant voltage less current will flow through the solution at the lower temperature. This means, therefore, that under the same conditions the current density, and therefore the rate of precipitation at low temperature at constant voltage, are lower than at higher temperatures. Therefore the crystals must be larger because the rate of deposition has a greater effect on the crystal size than the effect occasioned by the decrease in temperature, operating in the other direction. I have no doubt that if Mr. Hogaboom will take the trouble to measure the current and keep this constant, instead of the voltage, the crystal size of the deposited silver will be smaller at the lower temperature. We have checked this up from the standpoint of tensile strength in the case of copper. Copper deposited at low temperatures has a higher tensile strength than that deposited at higher temperatures, showing that the crystals are smaller.

With regard to the statement that the deposit is better when made from acid solutions, I cannot question this from the plater's standpoint. From the standpoint of theory, however, as is stated fully in the paper, a finer textured deposit, that is, a deposit made up of finer crystals, will be obtained from the alkaline solutions, under the same conditions of temperature, current density, etc.

Commercially, however, the conditions are quite different. The current density in acid solutions is very much greater than that in alkaline solutions, so that here again is introduced the effect of increased current density. The deposit from alkaline solutions may not be so pure as the deposit from acid solutions, which would, of course, introduce practical difficulties. The conclusion, nevertheless, remains that alkaline solutions under the same conditions will give finer crystalline deposits than acid solutions. From the standpoint of cost, of course, it will be impossible for the plater to use alkaline solutions altogether on account of the fact that the current density is low, and the work would have to remain in the bath for a long time.

The criticism which Mr. Hogaboom makes of the statement that iron contaminates the nickel bath is a perfectly logical one to be made by the practical plater of today on account of the fact that nickel anodes containing iron are used in practice. This use of nickel-iron anodes I will not admit as good practice. It has been found that iron in deposited nickel is a very important agent in causing it to peel (unpublished notes). The coating of the metal with copper, of course, prevents a reversal of the current and the solution of the metal, as is noted by Fontaine (Electrolyse, 2d ed., p. 78). If the plater were using practically pure anodes and practically pure solutions, the iron which might dissolve and be reprecipitated would prevent the adhering of the deposit. We have found in the laboratory that the best deposits are obtained by the use of electrolytic anodes with nickel ammonium sulphate as an electrolyte. A small amount of chloride is added, either as ammonium chloride or nickel chloride, to insure the quantitative solution of the anode. Under these conditions the deposit contains practically no iron, does not crack or peel off, and does not rust. At least, samples I had made some time ago have not rusted yet. Presumably, therefore, the pure metal gives a more resistant and a better grade deposit. If this fact is remembered by the platers here, and if they will attempt to use purer materials, we certainly should get a better grade of nickel deposited. Under theoretically ideal conditions, therefore, the contamination of the nickel bath by iron would be an important factor. The reason stated by Mr. Brown for plating iron objects with copper is not a theoretical one, but is merely a practical one.

Coating iron with copper to insure a clean surface seems to be a rather expensive substitute for the ordinary methods of cleaning. Why should not the plater, therefore, clean the material with greater care, so that the copper plating could be omitted?

Mr. Geo. B. Hogaboom: I ask if Mr. Bennett tried to melt the electrolytic nickel to cast it into anodes?

Mr. C. W. Bennett: We have not attempted to cast anodes, but we have melted electrolytic nickel and cast it into small test bars about half an inch in diameter, say, for corrosion tests. Electrolytic nickel can be purchased on the market containing 0.14 percent iron, average composition. When the metal is cast it will probably contain a little more, due to contamination from the containing vessel.

Mr. Geo. B. Hogaboom: A very large manufacturer of nickel anodes in this country bought several hundred pounds of electrolytic nickel and put it into the furnace and tried to melt it. It was impossible to do it unless an electric furnace was used. They lost a great deal of money through their experiments. We made some experiments; we wished to get a pure nickel containing no iron to alloy with gold, as a small percentage of iron in gold will make it crack. We talked it over, made some compositions with electrolytic nickel, and tried to melt them down without having an electric furnace; it was almost impossible.

Dr. W. D. Bancroft: I should say that this interesting experience we have just heard about furnishes an admirable illustration of the necessity of carrying on experiments on a laboratory scale before trying them commercially.

Prof. Jos. W. Richards: I do not know whether it is a suggestion worth while or not, but I thought that if the manufacturers of electrolytic nickel could be induced to deposit their electrolytic nickel in the shape of anodes it would avoid all the cost and impurities due to remelting.

Mr. C. A. Hansen: Electrolytic nickel can be satisfactorily melted in the arc type of electric furnace. We have melted it in 1,000-pound batches at a cost not exceeding $20 per ton. We deoxidized with small doses of aluminum or silicon, cast it into 4-inch and 6-inch ingots some 3 feet long, forged it into bars,

and used the bars. If the silicon or aluminum go higher than ½ percent, the metal pulverizes under the hammer.

Mr. Bennett presented the paper on "Electrodeposition of Brass and Bronze."

Mr. Geo. B. Hogaboom: What does Mr. Bennett mean by bronze? That is, would he expect an electrodeposited bronze to analyze up to regular bronze that you can cast?

Mr. C. W. Bennett: From a chemical standpoint bronze is an alloy of copper and tin. The two constituents may be present in varying proportions, and electrolytic bronze, therefore, would be any deposit of copper containing any amount of tin. In regard to the statement that no real bronze was being plated commercially it may be said that, with thanks to Mr. Hogaboom, who furnished me with addresses, something like 75 letters were sent to that number of platers' concerns requesting that they give the character and amount of plating they were carrying on with the solutions used. A number of formulæ for "bronze" solutions, so-called, were received, but these solutions invariably contained zinc instead of tin.

Mr. Geo. B. Hogaboom: In the Reading Hardware Company they run a bronze solution containing tin, and have done so for twenty years. George Irvin is the plater. You will find a description of that process in a review of the proceedings of the American Electro-platers' Society.

Mr. C. W. Bennett: I am very glad to hear of this, and will communicate with Mr. Irvin as soon as I return to Ithaca.*

Mr. Chas. H. Proctor: The electroplater in producing bronze tones naturally has always followed the process of making an alloy of copper and zinc. He has found that this solution is a good deal easier to handle than one with tin. Some time ago I was talking with a plater in Lancaster, Pa., and he told me that at the present time in the production of bronze deposit they are using nickel with the copper, and get very good results. It seems to me that nickel would naturally produce a very good bronze

* The bath used by Mr. Irvin contains copper and nickel. This information was very kindly furnished me by Mr. Hogaboom himself upon my return to Ithaca, so that it was unnecessary to communicate with Mr. Irvin. His process of bronze plating is published in the "Quarterly Review," National Electro-platers' Association, copyrighted, 2, Sept., Oct. and Nov., p. 27 (1911).—(C. W. B.)

tone. At the present time, the color of the deposit is sometimes regulated by the addition of arsenic; by using arsenic we get a more nickel-like structure, considerably darker than nickel. In depositing bronze upon hardware, we use a bath consisting of copper and zinc salts in a certain proportion, and then regulate the color by arsenic.

It seems to me that there could be a good deal of experimenting done with bronze solutions that would probably in the end produce very satisfactory deposits, and while, as practical men, we do not always have the time to go into this sort of thing, we do hope that you men who take such an interest in the electrolytic deposition of metals will solve these problems for us.

Dr. Edw. F. Kern: This discussion seems to bring out the fact that it is color which the practical electroplater produces and sells, and not an alloy deposit; whereas from the scientific side, the electrochemist wants an alloy deposit, which has a characteristic color.

Mr. Lawrence Addicks: It seems it is more or less the idea, as the electroplater puts it, that he should be able to sell zinc, bought at 6 cents, for tin at 50 cents.

Mr. Chas. H. Proctor: That is the commercial side of plating.

The Secretary presented Dr. Watts' paper on "Electrodeposition of Cobalt and Nickel."

Mr. Geo. B. Hogaboom: Speaking of the electrodeposition of cobalt and nickel, it may be interesting to bring out the fact that in experimenting with the enameling of agate ware, etc., it was found that if cobalt could be purchased cheaply enough, it would be much preferable to nickel as a coating under the enamel. At present very rich nickel solutions are used with a very high current, which "burns" the nickel deposit, making it come out black. I do not know what the current density is at which they operate the bath, but if you happen to touch the work against the anode, it will put a hole in the work, and crack it, the process is under such high pressure. The black deposit that is obtained is the base for the enamel coating and produces

what is known as nickeled steel agate ware. Experiments proved that the enamel would take better upon a cobalt deposit than upon a nickel deposit.

Mr. Lawrence Addicks: The situation in regard to cobalt, commercially, is very interesting. I understand that the International Nickel Company has withdrawn from handling it, and the market has gone to pieces. There is plenty of it. Some of the new copper fields in Central Africa carry a great deal of cobalt. There is considerable of it in Europe at the present time. The question which presents itself to us at the present time is how to get rid of the cobalt, and not how to save it. If anything can be done to make cobalt worth while, if it can be used commercially, there is almost an unlimited quantity of it that can be obtained. I do not know what price can be got. Cobalt is generally marketed as one of the three oxides, but could be readily produced as metal.

Mr. H. T. Kalmus: I should like to enlarge on the statement of the last speaker by saying that the Canadian Government has set itself the task of finding an outlet for the deposits of cobalt which are on hand in that country. The metal itself, I believe, can be made into castings for something like $1.00 a pound, which is not excessive. When I say that, I mean in moderate quantities, and if a market could be assured for large quantities, it might be considerably reduced. There is an accumulation of cobalt at the smelters in Ontario, which at the price mentioned would have a value of something between $10,000,000 and $15,000,000. You must remember that that is an accumulation which has been brought about in the working of the silver ores. If the platers have uses for cobalt, we should be glad to hear from them. The Canadian Government is spending over $10,000 a year in experimenting with cobalt to find uses for it, and the results have been very gratifying. Publications in detail will appear during the coming year.

Mr. Chas. H. Proctor: The reason we cannot use it is the price. Get the price down to that of nickel, and we can use it. Maybe it will give us a cheap nickel anode and enable us to bring our product down to a lower price.

Mr. Lawrence Addicks: What we need is some differentiation of the properties of nickel and cobalt. They are usually considered to be practically identical. If nickel can be purchased more cheaply than cobalt, cobalt is ruled out.

Mr. Geo. B. Hogaboom: I will state some of my experiences with cobalt and nickel deposition. I bought some sulphate of cobalt and paid $1.75 a pound for it and experimented with it in combination with nickel. I deposited some cobalt upon a piece of polished brass, and on another piece I plated from a solution of double sulphate of nickel, 8 ounces, sulphate of cobalt, 2 ounces, and chloride of ammonium, one-half ounce; this gave an elegant, bright deposit. I ran the deposit for two hours, straight, and it did not discolor. The objects which were plated were exposed to the elements all winter, and it was found that the cobalt changed its color and turned somewhat pinkish, while the cobalt-nickel did not change. Another thing about the cobalt-nickel deposit was that we could bend it, or twist it, without any danger of the deposit peeling. Samples were exhibited at the meeting of the American Electro-platers' Society. Whether that solution could be maintained so as to hold the same proportion of metal, is something I do not know.

Mr. F. A. Lidbury: Were any analyses made of the nickel-cobalt deposit to show if any appreciable amount of cobalt is deposited from the mixed solution? We know very little about the conditions of deposition of these two metals from solutions containing both, and it occurs to me that possibly from such a solution only nickel might have been deposited.

Mr. Geo. B. Hogaboom: The result was much different; it was almost silvery white. The South Bend Watch Company wants a very light deposit on their watch parts that would not tarnish. I suggested the cobalt-nickel bath to the plater, who tried it; he said it was the whitest deposit they ever obtained, but it was not satisfactory to the manufacturers; they wanted something more of a silvery color.

Mr. H. T. Kalmus: I deposited some cobalt-nickel alloys running as high as 20 percent in cobalt, and they are tougher than either the cobalt plate or the nickel plate deposited under corresponding conditions.

Dr. Edw. F. Kern: As a student I attempted to separate nickel and cobalt by electrolysis, and tried a number of different solutions, but in no case was I able to prevent the cobalt being deposited with the nickel. The ratio of cobalt to the nickel in the deposits was about the same in all cases as that of the two metals in the electrolyte. So it seems to me that if you wish to form an alloy deposit of nickel and cobalt it would only be necessary to use an anode of the composition you desire the metal to be deposited on the cathode, and also use an electrolyte which contains the nickel and cobalt salts in the same molecular proportion as the two metals in the desired deposit.

Mr. H. T. Kalmus: I wish to point out one or two matters which I think are becoming misunderstood. In the first place, cobalt can never compete with nickel as to price. When I said that cobalt, ultimately, with large orders, would more nearly approach nickel in price, I had in mind the ultimate possibility of working ores at present too lean in silver to pay, but which might be worked if their cobalt content had a market. I doubt if you can buy 10 pounds of 99.5 percent cobalt anywhere at any price just now; you can buy plenty of cobalt oxide. Over one-third of the output of the Canadian mines is utilized in the production of Co_3O_4, largely for the manufacture of blue coloring substances; the other two-thirds of the output is on hand. The total output is not comparable with that of nickel, and cobalt can probably never compete with nickel, pound for pound. We must find uses for cobalt, if we are to use it at all, such that cobalt will do things which nickel will not do; there is no use in trying to substitute cobalt for nickel, for I do not think you will be able to buy cobalt for much less than a dollar a pound for some time to come. Someone suggested that the Canadian Government might supply working samples for the electroplaters. I cannot represent the Canadian Government, but I am in charge of a department at Queen's University, Kingston, Ontario, which is experimenting for the Mines Branch of the Dominion Government. As a result I have on hand somewhere between 50 and 100 pounds of fairly pure metallic cobalt, and I would be glad to see that any plater who is interested in undertaking experiments on the use of cobalt is provided with a reasonable sample. On the other hand, I would be very glad if any of the platers, or anyone

else, who knows of work that has been done with cobalt, that is at all practicable, would advise me in reference to it. I hear occasionally of experiments, but find almost nothing in the literature which will give me any clew to the possible commercial uses of cobalt, so that no doubt we are doing things which have already been done and which have been filed away.

Mr. C. W. Bennett (*Communicated*): As to the question of electrodeposition of nickel from baths containing pure nickel salts, we have found some peculiar phenomena which we hope to report on later. Roughly speaking, the efficiency of deposition is proportional to the amount of ammonia at the cathode, up to a limiting value of course. The efficiency, on nickel ammonium sulphate solution, starts low and increases up to the maximum value as the alkalinity of the cathode compartment goes up. The efficiency reaches the maximum after a certain amount of ammonia is formed, and then begins to fall off. The deposition can be begun at any desired efficiency from the low value to the maximum by the addition of different quantities of ammonium hydroxide to the solution. This phenomenon of alkalinity at the cathode, when the efficiency is good, and when the deposit is best, seems to point to the fact that any iron which might be introduced at the anode compartment will be deposited as hydroxide before it reaches the surface of the cathode. It is very probable, therefore, that during the formation of a good deposit of nickel there is very little iron at the cathode, although we may be adding it at the anode continuously, so that, although the bath in the center may contain large amounts of iron, there may be a film over the surface of the cathode which is comparatively free from this metal, so that the addition of iron around the cathode, by solution of iron objects, for instance, may be of more or less importance.

The Secretary presented Mr. Frary's paper on the "Electrodeposition of Gold and Silver."

Mr. C. A. Stiehle (*Communicated*): I was very much interested in reading over the compilation of formulas collected by Mr. Francis C. Frary on the electrodeposition of gold, and found very few that are of any commercial use. In my thirty-

five years of experience in gold plating I have used some of those given in the paper, and will try to give the results of my experience.

The baths made with ferrocyanide are too unstable to be used in a commercial way, as they will not dissolve any gold from the anode, and therefore after using a short time become exhausted, and, as new gold cannot be added, have to be discarded, the gold recovered, and new baths made. About the only use that can be made of them is for gilding enameled work, as the enamel does not chip so easily in them as in the regular cyanide baths; but even for this purpose the cyanide bath, if properly proportioned and worked, is better.

The cyanide baths with the addition of other salts, such as sodium phosphate, sodium sulphate and caustic potash, work fairly well for a short time; then the work will become spotted or of a "foxy" color, and as a rule they cannot again be made workable.

A 10 percent gold chloride solution can also be used as a plating bath, but the metal deposited is spongy and has not a good color.

I have found that a good and practical gold bath, which always gives the same results, can be used indefinitely, and gives a deposit of any thickness from a flash to 1/32 of an inch (0.8 mm.), and good gold color, must contain nothing but the gold and cyanide. Either the potassium or sodium cyanide can be used, as the gold anode will dissolve in either one.

The gold may be put into the plating bath by electrolysis (by the porous cup method), and I have found that this is the very best method, although it takes more time than the following method; it always gives first-class results.

But I find it quickest and easiest to make the solution from fulminate of gold; this always gives good results. In dissolving the gold for fulminate, use about 3 oz. (90 cc.) of aqua regia to 15 dwts. (23 g.) of gold, and as soon as the gold is dissolved (there is no benefit in waiting until the chloride becomes syrupy) add about 2 quarts (1,900 cc.) of water, then 4 to 5 oz. (120 to 150 cc.) strong ammonia, which will precipitate the gold, filter and wash once with hot water, put into a vessel containing water in which the proper amount of cyanide has been dissolved, heated

to 160° to 180° F. (70° to 80° C.), and in a few minutes the fulminate will be dissolved and the bath ready for use. This bath may be used with as small an amount as 3 dwts. gold and ½ oz. of cyanide to the gallon (1.25 g. of gold and 3.75 g. of cyanide to the liter), when it will give a very light deposit, merely a flash, but a good gold color, in from 8 to 15 seconds, with 2 volts; or with as much as 25 dwts. of gold and 3 oz. of cyanide to the gallon (10 g. of gold and 22.5 g. of cyanide to the liter), with which I have deposited gold 1/32 of an inch (0.8 mm.) in thickness with a voltage of 0.5 to 0.8 in thirty-six hours. For a good color, such as is known as a Roman color, the bath should contain about 15 dwts. gold and 2 oz. of cyanide to the gallon (6 g. of gold and 15 g. of cyanide to the liter), the work to remain in the bath from three to five minutes at a pressure of 2 volts. There must never be too much free cyanide in the bath, as then the color of the deposit will be pale, and, where only light deposits are put on, the deposit may even, after disconnecting from the negative rod, be redissolved, and so much of the base metal to be plated may also dissolve before it is covered with the gold that the bath becomes contaminated thereby, which will result in poor color. There should be just enough free cyanide to dissolve enough gold from the anode to replace that which is taken from the solution. The appearance of the anode should always be clear and crystalline; if it becomes dark or black more cyanide must be added.

The anodes should always be fine gold and of the same surface area as the cathode, so that the gold in the solution can always be kept constant. I find that in plating with gold baths most platers think only a small anode surface is necessary.

This solution can be used indefinitely (with occasional filtering to remove organic matter) if it be not allowed to become contaminated with base metal. The solution I am now using I made three years ago, using it every day about eight to nine hours, and it gives as good results as when new. I deposit from 5 to 8 dwts. (8 to 12 g.) of gold out of it every day. These baths must all be worked at 160° to 180° F. (70° to 80° C.). For the carat gold solutions, such as 12 kt., 14 kt., red or green gold, I have found the best way to make them is to allow the anode, made of the proper carat and color, to dissolve into the bath electrolytically, as you then get the carat and color of the anode,

which, unless you are a pretty good chemist, cannot be done by introducing gold, silver, copper and cadmium as salts that dissolve in the cyanide solution; and it is a quicker way, as a bath can be made ready for use in from two to three hours. In these baths the gold content should be from 5 to 15 dwts. of gold and 5 to 8 oz. of cyanide to the gallon (2 to 6 g. of gold and 37.5 to 60 g. of cyanide to the liter), and the voltage should be from 4 to 8 volts; these baths can be used at a temperature of from 80° to 180° F. (30° to 80° C.).

Mr. Geo. B. Hogaboom: This day marks an epoch in the history of electroplating in this country, and the gentlemen who have compiled this collection of formulas should have the thanks of the American Electro-platers' Society for the very great service they have performed to the practical electroplater.

One of the greatest needs of the electroplating industry today is co-operation between the practical man and the electrochemist. One of the ways I think this can be accomplished is by having the universities that have courses in electrochemistry co-operate directly with the plater. This could be done by having some of these universities employ a practical man and put him in charge of the electroplating laboratory, under the supervision of the instructors. I know of young men who would be willing to enter the employment of some institution of learning for the sake of the education they would receive, provided they could get enough money just to live on for the time being. A man need not be engaged for an unlimited length of time, but be engaged for four or five years, until he had finished his course, and then another young man could step into his place. In that way you would educate the plater and gain the practical man's knowledge.

Another thing which should be arranged is some way by which the practical man could get in touch with the members of this Society. He can meet with platers and practical men and exchange ideas and experiences in regard to the everyday affairs of the plater, but if he only had the co-operation of the chemist to help him over some of his problems, look at the good which could be accomplished, for these things would be published and become public property.

The mere precipitation of metal from an electrolyte which con-

tains the metal is not, in the true sense of the word, as we would understand it, electroplating. To electroplate an object means more than to simply just coat it with the metal. You can coat aluminum with a metal, but the aluminum will not be electroplated. To be electroplated the surface must be thoroughly cleansed, it must be put into an active state so that the deposit will thoroughly adhere, the deposit must be smooth, it must be of a small, crystalline structure, in the case of silver it must be so that it is tractable to the burnisher, and it must be left in such shape that it can be easily polished on the wheel. It must also easily lend itself to any of the many decorations that may be called for, and for which not every deposited surface is suitable.

We will take the solutions one after another briefly, beginning with the nickel solution. There are about three classes of work which require nickel plating that differ from one another. First grey iron castings, such as stove work. Look at a stove casting and you will usually see highly polished nickel on the high lights and exceedingly white color in the deeper part, the background. The solution for such work must be able to deposit the metal heavily into every space on the article which is to be plated; a heavy deposit is required, and one that is perfectly white. In nickeling polished brass a different condition arises. This work must be plated so that there will be no white deposit whatever, so that after an hour's run the metal can be taken out of the solution so bright that it needs only to be wiped off to give it a brilliant color. A solution that will successfully deposit on iron work *can* be used to give the bright deposit on brass, but it is not the best. Finally for barrel plating, where a large number of pieces are put into a mechanical contrivance that rotates during electrolysis, and must all come out bright, an entirely different solution from either of the former two is required. It requires a solution that contains a large percentage of chlorine, so that it can throw the metal in, one that has a high specific gravity, and that can be operated under a higher pressure than any other solution. Thus there are three classes of nickel solution, and instead of saying in a general way that nickel can be deposited from a double-sulphate solution, or single-sulphate solution, with this or that added, a thorough investigation should be made to find just what solution is the best for each class of work.

Next, the gold solutions. Gold deposited on any surface reflects the color upon which it has been deposited. If you want a real yellow color, you can take a solution of cyanide of potassium and fulminate of gold containing, say, four pennyweights of gold to the gallon, and just enough free cyanide to give it action and operate it under a pressure of 1.5 volts. Plate with that on silver, you will get what is known as an 18-carat color; plate with it on brass you will get still another color, on copper still another. Plate with it on nickel and you get an exceedingly pale color. If the same solution be used for "inside work," that is, for plating the inside of a cream pitcher or sugar bowl, you will have a very poor color, "foxy," as it is called. A deposit that would look a nice orange color on inside work would look "brassy" anywhere else.

To obtain a "rose finish" you require a solution heavy in metal, very little free cyanide, and running under a higher pressure and even temperature. The shade must be uniform; the finish produced a year ago is brought up and matched with the finish produced today. You must operate the solution so that if you have 500 pieces finished, you can put the 500 pieces in a line and no one could pick out a single piece of a shade or color different from the rest.

To obtain green gold, one may use different proportions of gold and silver with either sodium arsenite or carbonate of lead, to produce the darker shades. Or the green gold anode can be cast and the gold "run in" with a porous cup. There are differences of opinion among platers as to the use of arsenic and lead, one prefers lead, the other arsenic. It is claimed that the atmosphere attacks the "arsenic" color more readily than the "lead" color.

Another gold solution referred to in the papers presented is the "sea water" or as it is more often called the "salt water" gold solution. This is made with the fulminate of gold, ferrocyanide of potassium and some sodium salts. A special apparatus is necessary and while no current from an outside source is necessary, it can be operated with it. This solution is used on the cheaper grade of novelty jewelry and can be operated very cheaply. One plater claims to have plated nine pounds of collar buttons with five pennyweights of gold.

The "dip" gold solution is also used for cheaper work. The articles are first "bright" dipped and then swilled in a boiling hot "dip" solution. The color appears very rapidly and the deposit is exceedingly light. At one time we "plated" some mesh bag frames four inches wide, a double chain, six inches in length, with a belt hook attached, for thirty-five cents a gross and made money. We used gelatin dissolved in hot water for a lacquer. This could not be accomplished at such a low price by electrodeposition, and have as uniform a color. It might be said that a gross of articles were dipped at once.

The plater in a factory where different classes of work are turned out is supposed to know every one of these solutions, and to be able to operate them successfully, day in and day out. They do not give you twenty-four hours to analyze a solution. They bring in a batch of work and say—we want that at such and such a time. If your solution does not work, you must make it work, and there is no opportunity for analysis. You must go ahead and do things.

Thirdly, the silver plating solutions, which are among the most simple to operate. Experience has shown that nothing but silver and cyanide should be added to the bath, but the solution must contain a sufficient amount of metal. A solution should contain approximately from 2.5 to 3 ounces of silver per gallon (18.5 to 22.5 g. of silver per liter) and should be operated under a pressure of one volt.

Now, when I speak of one volt pressure, of course, I know that from the point of view of the electrochemist I should say what current density is required. In the refining of metals, as in copper refining, where you can measure the cathode surface and the anode surface perfectly, and you know the density of the solution continually, and the temperature, it is all well and easy enough to say that the bath should be operated at a given current density for so many square decimeters of surface. In electroplating where the cathode surface changes continually and the anode surface remains practically the same, there should be some way of knowing whether you are getting the proper deposit or not. While it would be very nice to know how to figure out the proper current density to use, nevertheless, in practice it is almost an impossibility; and therefore the plater talks volts, and the volt

is the most important unit to the plater. He very, very seldom talks amperes. He knows that by regulating his anode surface so that he will get a pressure of a certain number of volts he is going to get a deposit, homogeneous and smooth.

The weight of the deposit is, of course, another important matter, and how much weight can be deposited in a given length of time depends on the solution. Now this solution may have been worked day in and day out all through the week; it can only be fixed up at the end of the week on Saturday afternoon or Sunday, so that very probably it does not contain as much metal or as much cyanide on Friday as it did on Monday. If the plater was capable of analyzing the solution and finding out how much metal and free cyanide there was in it, he could bring the solution to the proper composition, but he cannot; there is no laboratory in any plating room, outside of a few very large manufacturies. Every square foot of space is occupied and space costs money, so they cannot give a suitable place in which to put a balance and other necessary apparatus, and there is no time during the day to analyze solutions; the work must be got out.

Meetings like today can and will do much toward bringing about a better understanding of the electro-plating industry. If the manufacturer, the electro-chemist, the practical plater can be brought together more, each would receive benefits that would be of an infinite value. But first, start with the practical side that is beyond the experimental stage, and then work out new theories from what has been accomplished. Don't try to theorize the practical plater; rather make the electro-chemist a practical plater.

Dr. W. D. Bancroft: I have enjoyed Mr. Hogaboom's address very much, but he has not told us one or two things which, in my particular case, were the ones that I should really have liked to have heard. In the case of nickel plating he has told us that one must use different types of solution for plating the tops of stoves, for plating brass, or for use in the plating of steel. That is perfectly true, but it would help me a great deal more if he told what is undoubtedly perfectly obvious to him, that is, just why the deposit from one bath is not satisfactory in the other cases.

One solution was used for gilding the outside of a cream pitcher and another solution for the inside. There are more cross reflections on the inside of the pitcher, but I should like to be told more regarding the actual difference in the color of the gold and why in the case of these deposits the gold is just the right color you want on the outside and on the inside. I am willing to admit the fact, but when Mr. Hogaboom says that a solution "will not work," I would like to ask *why* it will not work. That is the thing on which I want help.

With all due respect, I would say one word about this difficulty of the chemist and the laboratory, of which Mr. Hogaboom gave us a very pathetic picture. It seems to me that the thing to do is to show the manufacturer that he cannot afford to go along in the present way, and that it will pay him to have a laboratory and to have his solutions analyzed. If it will not pay him, that is another matter; but as a chemist I think it would.

Mr. Geo. B. Hogaboom: For years all the plating has been done by men who have had no laboratory. If any plater should go to his employer and ask him to go to the expense of putting in a laboratory, the employer would laugh at him. The employer would say "We have had our work done satisfactorily for years, and we have had this proposition of a laboratory put up to us before, and we don't think there is much in it." I will give an illustration—there is a firm in Brooklyn, a well-known firm that does a great deal of silver plating work. The man in charge of the plating department asked for a voltmeter. They said to him: "We have been doing silver plating for twenty-five years, and we have never had a voltmeter in the place. What do we need a voltmeter for? Our work has always been satisfactory."

I will give you one more instance. Suppose I were to tell you that one of the largest manufacturers of electrical instruments in this country did not run his plating room upon a chemical basis? He would not think of employing anybody but a thoroughly educated electrical engineer in his electrical laboratory. Still I have known of his putting in a man as head plater who did not know the first principles of chemistry. I have known of that man buying 100 pounds of carbonate of soda and throwing the whole into a sulphate of nickel solution to make it more alkaline. This

manufacturer will employ only electrical engineers for the electrical end, but in the plating room he employs men who do not know anything at all about chemistry.

As far as the two colors are concerned, gold inside and outside, the reflection of light upon gold has a great deal to do with the color. If you deposit gold inside a cream jug, the light is all reflected in, and it will be an orange color. If you plate with the same solution on the outside where the light is diffused, the color of the underlying metal will show through, for gold deposited from a solution is translucent, and a different color will result. Thus if you first coat the outside with copper, then gold plate it, you can match the inside very easily, but if you plate the outside directly on the silver you will not and cannot get the same color.

A very highly polished piece of brass work does not require as heavy a deposit of nickel as a piece of grey iron. A half-hour deposit is sufficient and the work will only need a light coloring with a buff. On grey iron the surface is dull and consequently the deposit of nickel will be dull and the brilliancy of the deposit can only be obtained by polishing with a rag or a felt wheel, using "lime" for the abrasive. There is some work that has to be done very cheaply and a large amount of it must be turned out so that it will pay. A three-hole gas hot-plate, such as is ordinarily used, must be taken as it comes from the foundry, polished, nickeled and colored for about 23 cents; this must include the legs and the white nickeling of the grates.

Mr. P. S. Brown: I sincerely hope that this discussion will lead toward a better co-operation and better feeling between the electrochemist and the plater, but I do not agree with Mr. Hogaboom that the solution of the difficulties is to submit samples of the materials for analysis, because the chemist's time is worth money. What the electroplater must do is to convince the manufacturer that the chemist is needed now and then, and let the manufacturer pay for the services of the chemist; even if he does not put in the equipment, let him send the samples out to the chemist and have the work done, because I can see if you once encourage the foremen electroplaters to submit samples, every chemist in the United States will be swamped within six months.

No doubt there are many problems that we would like to solve, but we must go at their solution in a rational way.

As to this case of voltage and amperage, I believe that is a matter of information; in other words, the chemist and the electroplater need standardizing as much as the machine shop. I have had some experience in standardizing electroplating departments, and in some cases have been able to put all the work on a piece-work basis. The average plater would think that was impossible; he would think that if a man wanted to shirk his work, or soldier, all he need do is to take out the racks a little quicker. This difficulty was overcome by insisting that every piece of plated ware that goes out of the department must meet a specific test for the quantity of nickel or silver or copper per square inch of plated surface; so many pieces are tested every day from every lot of work, a square inch of the nickel being removed and analyzed by a simple method which allows a great many of these tests to be made in a day. On such strong individual testing lies the ability to systematise the department. Assume that you want eight loads a day of a certain material, and you want the eight loads absolutely standard in quality and the same from one day to the other the year round. In such a case it is possible to make out an individual card for every part that goes through. That card gives the rack on which the part shall be placed, tells how many pieces to put on the rack, how many racks are to be put in the tank, and it then tells how many amperes must go through these racks and how long. If it says 300 amperes for thirty minutes, they must stay in thirty minutes and get the 300 amperes. If by chance the man who is in charge of the solution fails in his job, lets the solution get away from his control, the work may be spoiled under the conditions of current prescribed, because in efficient work you work close to the maximum possible rate of deposition. If the solution is low in metal, a current that normally might require three volts would perhaps need 4.5 volts, and at the end of twenty-five minutes the work might be burned on the edges. That would be the fault of the solution expert, because he should be able to tell by a comparison of the actual voltage with that on the card whether or not his solution is in proper working order.

In this method of working, the proper voltage is entered on the cards merely as a control of the condition of the solution. It

is probably less applicable in silver and gold plating than it is in the plating of ordinary metals, but there are undoubtedly establishments today that are using the same method in silver plating.

PROF. JOS. W. RICHARDS: I think Mr. Bancroft has asked too much of Mr. Hogaboom when he asked him to tell him *why*. The way I view it is that the plater with practical experience will have to provide the facts which are lacking to the scientific man, and after the scientific man has these facts *he* must tell the practical man *why* they are so.

In regard to Mr. Hogaboom's suggestion that electroplating establishments might be established at the universities, I wish to venture a different opinion. I do not think the university is the place to teach men the practical details of the trade, but a place for a man to study and get the principles. I do not think that anything could be better for a student who desires to be a plater than to spent a year in the plating works before going to the university, and then afterwards following up the knowledge which the university has given him by the practical application of this knowledge to actual work.

The Secretary presented Dr. Mathers' paper on "Electrodeposition of Lead."

DR. W. D. BANCROFT: The question of "addition agents" is brought prominently before us by this paper. In some cases the effect can easily be explained, as where colloids are carried to the cathode, and gelatine, etc., is used to prevent crystallization. There are other substances, however, such as oils, which when added to the solution have a very marked effect. From the point of view laid down in the "Axioms of Electroplating," which I distributed, it follows that these substances, in order to act as they do, must be adsorbed by the metal. For fear some person might turn around and say, "You are simply inventing that hypothesis in order to rescue your theory," one has to get some other way of showing the adsorption, apart from the electrochemical side.

Such independent evidence is suggested by the work which has been done in the last eight or ten years on the flotation of ores, where you treat a zinc sulphide ore with oil in an acid

solution. I wished to show my students an experiment illustrating this, and therefore shook finely-divided copper and a little quartz sand with kerosene oil and water. The copper went to the top, and the sand remained at the bottom. On tipping the bottle [*demonstration*] you will find in a moment or two that the oil carries the metal up again. The same principle is involved in the bronzing liquids. They contain aluminum powder or copper powder, for instance, with amyl acetate, in case you want an expensive one, or kerosene and resin, in case you are economizing; but the essential thing is that they hold the metal up, which proves that the metals adsorb these liquids. I have no doubt but that Dr. Mathers would find, if he shook up his powdered metals with different oils, that oil of cloves, which is the best one to use in electrolysis, would prove to be the best for suspending the metal. I believe that the flotation of ores, the behavior of bronzing liquids and this electrodeposition of the metals in the presence of these oils all depend upon the same general principle; all that is necessary in these cases is to use an oil or other substance, which is carried to the cathode and which is adsorbed by the metal, and it will then prevent the growth of large crystals.

Mr. N. S. Keith: In connection with the use of addition substances I recall that quite early in the 70's, in a nickel-plating establishment, I discovered that one of the platers was in the habit of chewing tobacco and squirting the tobacco juice into the solution. When I took him to task he said he found it gave good results. There was certainly organic matter put into the solution with a vengeance.

This seems to be an opportune time to correct the statements which have been made on page 170 of Mr. Mathers' paper, not on his own authority, but quoted from former publications, as stated. The original publication (Eng. Min. J. **26**, 26, 1878) was based upon my United States patent, October 15, 1878, No. 209,056. This was followed by my United States Patent, May 20, 1879, No. 215,463.

This latter patent claimed among others, an electrolyte composed of lead sulphate dissolved in a solution of sodium acetate. This latter electrolyte had been found much superior to the former

one in the fact that the acid solution could not in practice be kept of constant composition, because more lead was dissolved from the anode than was deposited on the cathode, thus neutralizing the free acid. Then followed the formation and deposition on the anode of lead peroxide; subsalts dissolved in the electrolyte, with increased resistance and polarization in the cell circuit. If acid were added to preserve the integrity of the electrolyte, an accumulation of dissolved lead salt necessitated other manipulations for the recovery of the lead therein. The case is different with the electrolyte consisting of lead sulphate dissolved in the sodium acetate solution. The crystals of lead are much coarser and more coherent than those produced in an acid solution. They remain untarnished in the electrolyte for a long time. Several pounds of these crystals in a large bottle filled with some of the electrolyte, which were exhibited at the electrical exhibition of the Franklin Institute in Philadelphia in 1884, were bright and uncorroded more than a year thereafter.

During the time of the exhibition, namely, September, 1884, I read before the Philadelphia meeting of the American Institute of Mining Engineers a paper describing the process and the apparatus therefor then established at Rome, New York. That lengthy paper seems to have been overlooked, purposely or otherwise, by those who have been interested enough to print alleged descriptions of the process and their comments and deductions thereon. Those who are sufficiently interested may find the paper in the Transactions of the American Institute of Mining Engineers for the year 1884. See also "Electrolytic Separation of Metals," by Gore, 1890, pp. 244-5-6-7, for purity of the refined lead.

I have with me two discs made by compressing some of these crystals in 1883. It will be observed that these discs are metallic, and only superficially corroded, as any piece of lead might be which has been exposed to the action of the atmosphere of many climes for thirty years.

The process and the apparatus, etc., were fully described in the paper published in the Proceedings of the Mining Engineers in 1884; it went out of use mainly because it was so early in the electrolytic art, I think, that they could not induce the leading refiners to adopt it. They used the zinc process of separation,

and have in great measure continued it, though some are using the Betts electrolytic process and using it very successfully. I think, however, that the acetate solution can be used under the methods now pursued with equal efficiency at least; it is free for all who wish to test it.

Dr. W. Lash Miller: It is with great pleasure that we hear these remarks from Dr. Keith, who, as is well known, is one of the pioneers in the electrolytic industry.

Mr. Chas. H. Proctor: The only use we electroplaters have for the deposition of lead is in the production of what is commercially termed Royal Copper—this is the beautiful pigeon-red color resembling enamel noted upon cases of electrical measuring instruments such as made by the Weston Electrical Instrument Company and as a finish upon art metal goods. In using lead solution for the purpose we use nothing more than the common solution of acetate of lead and caustic soda. The idea of getting this film of lead on the copper surface is to prevent oxidization previous to the immersion in the molten solution. We produce this oxidization by immersing in potassium nitrate, and protect the copper surface from the moisture and atmospheric influence previous to the immersion by coating it with lead. The only other instance I know of where lead is used is for the production of what we term "Metallo-chromes," or iridescent colors by reverse current. I do not think that our members can enter into any discussion on the electrodeposition of lead.

Dr. Kern presented his paper on the "Electrodeposition of Tin."

Mr. A. S. Cushman: I have been using an electrolytic method for determining tin in canned foodstuffs. I adopted this method as a very rapid and convenient way of determining very small amounts of tin in the presence of an excess of organic matter. You are probably aware that under the food inspection decisions of our Government any tinned goods are liable to condemnation that contain more than 300 milligrams of tin salts per kilogram of the packed food.

I have had charge of an investigation in which a very large number of cans, representing all the ordinary foodstuffs packed in tin, were put up under test conditions. This necessitated the

determination of tin salts in a great many hundreds of samples of different sorts of foods. The old-fashioned method for the determination of tin in a material of this kind called for the complete destruction of the organic matter by the introduction of nitrosulphuric acid. This was an expensive process, destructive to laboratory flues and hoods, etc., and consumed a great deal of time.

By means of the electrolytic method we can now turn out 30 tin determinations a day. The method has already been published, so I need not describe it at this time. (Journal of Industrial and Engineering Chemistry, **5**, No. 3, 1913.)

You may be interested in hearing of one or two of the points that have been developed by these investigations. In the first place, it would seem probable that those fruits and vegetables which are most acid would be most highly contaminated with tin salts; that is not invariably found to be the fact. Tomatoes are quite an acid vegetable, as everyone knows, and yet tomatoes come very well within the limit of 300 milligrams per kilogram, even after two years' enclosure in the can. Tomatoes rarely run over 100 milligrams per kilogram, whereas squash, which is a neutral vegetable, will practically detin a can inside of a year. The reason for the fact that most acid fruits do not always take off the most tin seems to lie in the fact that there are other organic bodies that have a much higher solvent or corroding power on tin than the dilute organic acids have. For instance, shrimps and some other shell fish are very destructive to the tin containers in which they are packed. This is believed to be due to the action of certain nitrogenous or amido bodies contained in or developed by the fish.

Perhaps the most interesting point developed in these researches is the following: For years it has been the practice among canners to specify different weights of tin coating on the sheet from which the cans are made, and they have the choice of three separate grades of tin. These grades are sold under the designations "charcoal" plate, "coke" plate and "canners' special," the charcoal carrying the heaviest weight of tin, the canners' special second, and the coke the lightest.

Among the very great number of test cans to which I have referred we had a number of cans made of these three different

grades of tinplate, and in almost every case where the results were scrutinized it was seen that there was no advantage to be gained by selecting the heavy tin coating for packing food. This is one of the very rare examples of a case where the cheapest way of doing a thing is as good as the most expensive.

A paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 3, 1913, President W. Lash Miller in the Chair.

CONVECTION AND RADIATION OF HEAT.

By Irving Langmuir.

Part I: Historical.

Dulong and Petit, in 1817 (Ann. de chim. et de phys. **7** (1817)), published the results of extensive experiments on the rate of cooling of heated bodies in air. Most of their work was confined to the rate of cooling of thermometer bulbs in hollow metal vessels.

They recognized that the heat loss was due to two distinct causes, radiation and convection. The radiation they found to depend only on the nature of the surface and on the temperature of the body and its surroundings, and not on the shape of the body. The convection depended on the temperature of the body and its surroundings and upon its shape and position, but was independent of the nature of the surface. They summarized their results by the purely empirical formula:

$$\mathbf{W} = ma^{\delta}\left(a^{T} - 1\right) + nT^{b}$$

The first term gives the radiation, and the second term the convection. The symbols have the meaning:

$\mathbf{W}$ = heat loss per square cm. per second.
δ = temp. of the air in °C.
T = temp. of the body above that of the air.
m = a constant, depending on the nature of the surface of the body.
n = a constant, depending on the shape and position of the body.
a = 1.0077, constant for all bodies under all conditions.
b = 1.233, constant for all bodies under all conditions.

Dulong and Petit did not determine the numerical values of m and n for bodies of much practical interest.

E. Péclet (Traité de Chaleur, 3rd Ed., Paris, 1860) made perhaps the most elaborate and thorogoing experiments that have yet been made on the heat losses from surfaces. He concluded that Dulong and Petit's equations were accurate and that the values of the constants a and b given by them were reliable. Péclet determined with great care the numerical values of m for various kinds of materials and the values of n for bodies of various simple geometrical shapes. His experiments (see Paulding's translation of Péclet's work, Practical Laws and Data on the Condensation of Steam in Covered and Bare Pipes, C. P. Paulding, Van Nostrand Co., 1904) consisted in measuring the rate of cooling of hollow metal cylinders, spheres and prisms filled with water. Great care was taken to keep a uniform temperature in the vessels by means of elaborate stirring devices. He used bodies ranging from 5 to 30 cm. in size. These bodies were placed in a large water-jacketed metal cylinder about 80 cm. in diameter and 100 cm. high. He apparently assumed that the temperature of the air around the hot body was the same as that of the water in the large cylinder.

Dulong and Petit's formulas, as supplemented by Péclet's work on the variation of n with the dimensions of the body, have been and are still taken, in engineering practice, as an accurate expression for heat losses from surfaces. It has usually been found that the loss by convection calculated from Péclet's formulas is too low, but this has been taken care of by using values of n about 25 percent higher than those given by Péclet. No one seems seriously to have questioned the accuracy of the form of the equation as devised by Dulong and Petit.

In general practice, engineers have usually been content to assume that the heat loss from a surface is proportional to the extent of the surface and to the difference of temperature between the body and its surroundings. In many cases this simple method has been found just as accurate in practice as the more complicated formulas of Péclet.

According to Péclet the heat loss by convection is not proportional to the surface, but increases more slowly even for bodies of fairly large size. For example, Péclet's formulas give for the energy loss by convection from spheres and cylinders of various sizes the values shown in Table I.

TABLE I.

Watts per sq. cm. Loss by Convection.

Room Temperature 27 °C. Temperature of Body 127 °C.

Diameter Cm.	Horizontal Cylinder		Sphere	
	Péclet	Langmuir[1]	Péclet	Langmuir[2]
∞	0.038	0.060	0.033	0.060
100	0.040	0.061	0.039	0.061
10	0.053	0.066	0.082	0.071
1	0.182	0.104	0.527	0.152

[1] Calculated from equations (17) and (16), taking B = 0.465 cm. and $\varphi_2 - \varphi_1 = 0.028$.

[2] Calculated from equations (23) and (22), taking B = 0.465 cm. and $\varphi_2 - \varphi_1 = 0.028$.

For vertical planes the corresponding values are given in Table II. It will be observed that the watts lost per sq. cm. from a surface 1 meter high, according to Péclet's formulas, is 21 percent greater than the loss per sq. cm. from a surface 10 meters high.

TABLE II.

Watts per sq. cm. Loss by Convection from Vertical Plane Surface. According to Péclet.

Room Temperature 27 °C. Temperature of Body 127 °C.

Height of Plane in Cm.	Watts per Square Cm.
∞	0.033
1000	0.037
100	0.045
10	0.070
1	0.152

Many attempts have been made on the part of physicists and mathematicians to develop the theory of the convection of heat. In all cases it has been necessary to make simplifying assumptions in order to get equations which can be handled mathematically. These assumptions have very seriously restricted the usefulness of the results. A review of this work on heat convection and references to most of the important work on the subject

will be found in a recent paper by Alex. Russell (Phil. Mag. **20**, 591 (1910)).

The author as far back as 1905 felt that in the immediate proximity of hot wires the heat must be carried almost solely by conduction, and that the amount of heat carried by convection must be very small. More recently he attempted to determine how thick a film of stationary gas around a wire would make the heat loss equal to that actually observed. That is, he assumed that around a wire there is a cylindrical film of gas of definite diameter, thru which the heat is carried only by *conduction* and outside of which there is no appreciable temperature gradient, the heat in this outer zone being carried entirely by *convection*. This hypothesis, when tested by extensive experiments on the heat losses from heated platinum wires, led to very interesting and useful results (Phys. Review, **34**, 401 (1912)). The results were further tested (Proc. A. I. E. E., **31**, 1011 (1912)) by applying them to Kennelly's (Trans. A. I. E. E., **28**, 363 (1909)) data on the "Convection of Heat from Small Copper Wires."

It is the object of the present paper to extend the work of the two preceding papers to cover convection of heat from plane surfaces. Altho with wires the radiation of heat is practically negligible compared to convection, the reverse is often the case with plane surfaces, and therefore, in considering convection from such surfaces, it will also be necessary to take into account radiation. In this paper it is also intended to summarize the previous results and put them into such practical form that they will be of service in actual problems in heat transmission from surfaces.

Part II: Theoretical.

It will be assumed that the heat loss from any surface is the sum of two parts, radiation and convection. Thus:

$$\mathbf{W} = \mathbf{W_R} + \mathbf{W_C} \qquad (1)$$

where **W** is the total heat loss in watts per sq. cm. The Stefan-Boltzman Law[3]

$$\mathbf{W_R} = 5.9 \times 10^{-12} (T_2^4 - T_1^4) \text{ watts per cm}^2 \qquad (2)$$

gives accurately the rate of heat loss from a *black body* at the temperature T_2 in surroundings of the temperature T_1.

[3] Gerlach, Ann. Phys., 38, 1 (1912).

For any other body we may put

$$\mathbf{W_R} = 5.9\, E \left[\left(\frac{T_2}{1000}\right)^4 - \left(\frac{T_1}{1000}\right)^4 \right] \tag{3}$$

where E is the emissivity of the body. The quantity E is a number which must always be less than unity, and will be different for different substances. For most materials E will vary only very slightly with the temperature, and may, for practical purposes, usually be considered a constant for any one substance.

We will assume that the heat loss by convection $\mathbf{W_c}$ consists essentially of heat *conducted* away from the body thru a film of relatively stationary gas around the body. We assume that the temperature of the outside surface of this film is the same as that of the gas at a great distance from the body, that is, that the whole of the temperature drop occurs with the film.

The problem of heat convection thus reduces to one of heat conduction.

In all problems of heat conduction we may obtain a formula of the form

$$W = S \int_{T_1}^{T_2} \mathbf{k}\, dT \tag{4}$$

where W is the total watts of heat flow. S is what we may call the "Shape Factor," and $\mathbf{k}$ is the heat conductivity of the material at the temperature T in watts per cm. per degree.

The shape factor depends only on the geometrical shape of the body and the positions of the surfaces by which the heat leaves and enters the body. There are only three simple cases in which the shape factor can be rigorously calculated. In a subsequent paper it will be shown how it may be calculated with a considerable degree of accuracy for several other cases occurring commonly in practice. The three simple cases are for flow of heat between

(I) Parallel plane surfaces

$$S = \frac{A}{t} \tag{5}$$

where A = area of surface
t = thickness of material between surfaces.

(II) Concentric cylinders

$$S = \frac{2\pi l}{ln \frac{b}{a}} \tag{6}$$

where l = the length of the cylinder, b and a are the diameters of the outer and inner cylinders, respectively.

(III) Concentric spheres

$$S = \frac{2\pi}{\frac{1}{a} - \frac{1}{b}} \tag{7}$$

where b and a are the diameters of the outer and inner spheres, respectively.

For convenience we may place

$$\begin{aligned} \varphi_1 &= \int_0^{T_1} \mathbf{k}\, dT \\ \varphi_2 &= \int_0^{T_2} \mathbf{k}\, dT \end{aligned} \tag{8}$$

Equation (4) then reduces to the form

$$W_c = S\,(\varphi_2 - \varphi_1) \tag{9}$$

In all problems in heat conduction where the heat conductivity varies with the temperature it will be found convenient to use equation (9). Tables or curves of φ as a function of the temperature can be prepared for any case, and it will be found much more satisfactory to use these than to use a mean value of the heat conductivity for the temperature range in question.

We will now return to our problem of heat convection. Let us consider first the case of a plane surface.

Convection from a Plane Surface.

We have here to consider the heat conduction thru a plane film of gas adhering to the surface. Let us call the thickness of this film B, then we have

$$W = \frac{A}{B}\,(\varphi_2 - \varphi_1) \tag{10}$$

or, if we represent the watts per sq. cm. by $\mathbf{W}_c$,

$$\mathbf{W}_c = \frac{1}{B} (\varphi_2 - \varphi_2) \tag{11}$$

Convection from Cylindrical Wires.

In this case the wire (of diameter a) is surrounded by a cylindrical film of gas of diameter b. The thickness of the film is thus $\frac{1}{2}(b-a)$. We then have

$$W = \frac{2 \pi l}{ln \frac{b}{a}} (\varphi_2 - \varphi_1) \tag{12}$$

It would naturally be supposed that the thickness of the film $\frac{1}{2}(b-a)$ would be a function of the size of the wire. The most reasonable assumption in this case is that not only the temperature, but also the temperature gradient at the outside surface of the film, would be the same as in the case of the film adhering to the plane surface. If we let r be the distance from the axis of the wire to any given isothermal surface, and x the distance of the corresponding isotherm from the surface of the plane, then we have, since the temperature gradients are to be the same,

$$dr = dx$$

at the outside surfaces of the films. With equal gradients the heat flux per unit surface would also be equal at the outer surfaces of the two films. Within the films, however, the heat flux density would remain constant in case of the plane film, but would vary inversely as the radius r in the case of the wire. The distance between corresponding isotherms would be inversely proportional to the heat flux density, therefore directly proportional to the radius in the case of the wire. That is, dr is proportional to r. But when r equals $\frac{1}{2}b$, dr and dx are equal, therefore

$$dr = \frac{r}{\frac{1}{2} b} dx \tag{13}$$

or

$$\frac{dr}{r} = \frac{2\, dx}{b}$$

Integrating the first term between the limits $\frac{1}{2}a$ and $\frac{1}{2}b$, and the second term between the corresponding limits 0 and B (B being the thickness of the film for a plane surface), we obtain:

$$ln \frac{b}{a} = \frac{2\ B}{b} \tag{14}$$

This equation enables us to calculate b from B. We can save an extra operation by expressing the shape factor S directly in terms of a and B. To do this, substitute (14) in (6) and obtain

$$S = \frac{\pi\ b\ l}{B} \tag{15}$$

but from (6)

$$ln \frac{b}{a} = \frac{2\ \pi\ l}{S}$$

whence

$$b = a\ e^{\frac{2\ \pi\ l}{S}}$$

substituting this in (15)

$$S = \frac{\pi\ l\ a}{B}\ e^{\frac{2\ \pi\ l}{S}}$$

If we place $\frac{S}{l} = \mathbf{S}$, the specific shape factor or shape factor per cm., we have

$$\frac{a}{B} = \frac{\mathbf{S}}{\pi}\ e^{-\frac{2\ \pi}{S}} \tag{16}$$

For numerical calculations, a/B can be plotted as a function of $\mathbf{S}$, and from this curve the shape factor for a wire of any given diameter can be found when the value of B, the film thickness for a plane surface, is known. The energy loss per cm. $\mathbf{W}_c$) will then be

$$\mathbf{W}_c = \mathbf{S}\ (\varphi_2 - \varphi_1) \tag{17}$$

A table of $\mathbf{S}$ as a function of a/B is given in Table III.

Convection from Spheres.

In this case the sphere (of diameter a) is surrounded by a spherical film of gas of diameter b. The thickness of the film is thus $\frac{1}{2}(b-a)$. We can carry thru the same train of reasoning as in the case of the cylindrical wires and so obtain in place of (13):

$$dr = \left(\frac{r}{\frac{1}{2}b}\right)^2 dx \tag{18}$$

Integrating as before and dividing by 2:

$$\frac{1}{a} - \frac{1}{b} = \frac{2\,B}{b^2} \tag{19}$$

By combining this with (7) we get:

$$S = \frac{\pi\, b^2}{B} \tag{20}$$

Substituting this in (19):

$$\frac{1}{a} - \sqrt{\frac{\pi}{S\,B}} = \frac{2\,\pi}{S} \tag{21}$$

From this S can be plotted as a function of a, or the equation can be solved, giving:

$$S = \frac{\pi\, a^2}{2\,B}\left(1 + \frac{4\,B}{a} + \sqrt{1 + \frac{8\,B}{a}}\right) \tag{22}$$

TABLE III.

Shape Factor for Wires.

S	a/B	S	a/B	S	$a\,B$	S	a/B
0.0	0.0	5.0	0.453	10	1.696	30	7.738
0.5	0.56×10^{-6}	5.5	0.558	12	2.263	32	8.370
1.0	0.594×10^{-3}	6.0	0.671	14	2.844	34	8.995
1.5	0.725×10^{-2}	6.5	0.788	16	3.438	36	9.622
2.0	2.752×10^{-2}	7.0	0.908	18	4.040	38	10.25
2.5	0.0644	7.5	1.032	20	4.645	40	10.87
3.0	0.1176	8.0	1.160	22	5.263	42	11.50
3.5	0.185	8.5	1.291	24	5.877	44	12.14
4.0	0.265	9.0	1.424	26	6.505	46	12.77
4.5	0.354	9.5	1.561	28	7.122	48	13.40
5.0	0.453	10.0	1.696	30	7.738	50	14.03

The heat loss by convection from the sphere then becomes:

$$W = S\,(\varphi_2 - \varphi_1) \tag{23}$$

In the case of the sphere we may also calculate the convection if we know B, the film thickness for a plane surface.

Value of B, Thickness of Plane Film.

For both the cylinder and sphere the thickness of the film can be readily calculated if we know its thickness for a plane surface. Any experiment on the convection of heat from planes or cylinders thus furnishes us a means of calculating B. If the above assumptions are substantially correct, then we should obtain the same values of B from experiments on wires of any size, as we obtain from plane surfaces. We may further determine how B varies with the following factors:

1. Temperature of the hot body.
2. Position of the hot body.
3. Temperature of the surrounding gas.
4. Pressure of the gas.
5. Velocity of the gas.
6. Composition of the gas.
7. Nature of surface.

In the experimental part of this paper the effects of these factors on the values of B will be discussed in detail.

Calculation of φ, the "Thermal Conduction."

It is shown in the previous paper that the variation of the heat conductivity of any ordinary non-dissociating gas can be expressed by the equation:

$$\mathbf{k} = A\,(1 + \alpha T)\,\frac{\sqrt{T}}{1 + \dfrac{C}{T}} \tag{24}$$

C is Sutherland's constant, α is the temperature coefficient of the specific heat of the gas. From this we obtain as a very close approximation by (8):

$$\varphi = A\,(1 + 0.6\,a\,T) \int_0^T \frac{T^{1/2}\,dT}{1 + \frac{C}{T}}$$

The integral has the value

$$\frac{2}{3}\,T^{3/2} - 2\,CT^{1/2} + 2\,C^{3/2}\,tan^{-1}\sqrt{\frac{T}{C}}$$

Table IV gives the values of A, a and C for several of the common gases.

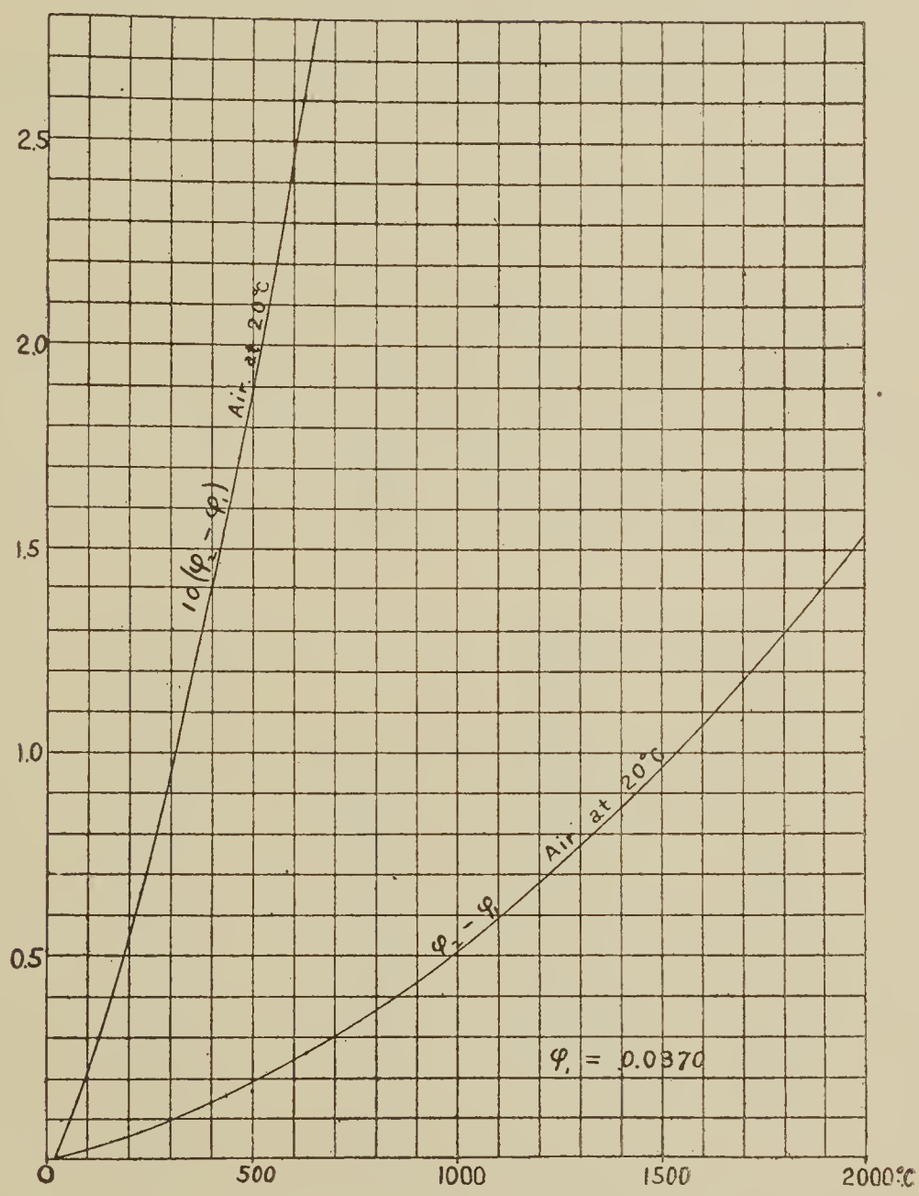


FIG. 1.

Plot of $\varphi_2 - \varphi_1$ for air; Abscissae, Temperature of Hot Body in °C.; Ordinates, $\varphi_2 - \varphi_1$. Room Temperature (T_1) is taken as 20 °C.

Table IV.

Data for Thermal Conduction of Gases in Watts per Cm. per Degree.

Gas	A	a	C
Air	19.2×10^{-6}	0.0002	124
Hydrogen	117.0×10^{-6}	0.0002	77
Mercury vapor	10.0×10^{-6}	0.0000	960
Nitrogen	19.9×10^{-6}	0.0002	110
Carbon dioxide below 1,100° K.	13.1×10^{-6}	0.00095	260
Carbon dioxide above 1,100° [4]	20.9×10^{-6}	0.00026	260

[4] According to Pier, Z. f. Elektrochem., **16**, 899 (1910), the mean specific heat of CO_2 from 0° C. can be well represented by a line broken at 1,100°. Thus for the molecular specific heats of CO_2 at constant volume we take

Below 1,100° K. $C. = 5.45\ (1 + .00095\ T)$ g. cal per °C.
Above 1,100° K. $C. = 8.68\ (1 + .00026\ T)$ g. cal per °C.

The values of φ calculated for temperatures above 1,100° K. have all been diminished by .415, in order that there may be no break in the curve at 1,100° K.

From these data the values of the thermal conduction φ for these gases have been calculated (slide rule) and are given in Table V.

Table V.

Table of φ, in Watts per Cm., as Function of Absolute Temp. (°K.).

T	Air	Hydrogen	Mercury Vapor	Nitrogen	Carbon Dioxide
0° K.	0.0000	0.0000	....	0.0000	0.0000
100°	0.0041	0.0329	....	0.0054	0.0036
200°	0.0168	0.1294	....	0.0188	0.0082
300°	0.0387	0.278	....	0.0417	0.0207
400°	0.0669	0.470	....	0.0717	0.0390
500°	0.1017	0.700	0.0165	0.1081	0.0635
700°	0.189	1.261	0.0356	0.1989	0.1318
900°	0.297	1.961	0.0621	0.3119	0.2274
1,100°	0.426	2.787	0.0941	0.4450	0.3620
1,300°	0.576	3.726	0.1333	0.5980	0.5455
1,500°	0.744	4.787	0.1783	0.7710	0.7325
1,700°	0.931	5.945	0.228	0.9620	0.9370
1,900°	1.138	7.255	0.284	1.172	1.117
2,100°	1.363	8.655	0.345	1.401	1.363
2,300°	1.608	10.18	0.411	1.649	1.634
2,500°	1.871	11.82	0.481	1.918	1.932
2,700°	....	13.56	0.556	2.202	....
2,900°	....	15.54	0.636	2.511	....
3,100°	....	17.42	0.719	2.834	....
3,300°	....	19.50	0.807	3.176	....
3,500°	....	21.79	0.898	3.540	....

The results for air are also given by the curve in Fig. 1. For convenience the temperatures are given in Centigrade degrees and the value of φ for a temperature of 20° C. (that is, $\varphi =$ 0.0370) has been subtracted.

Part III: Experimental.

The experiments on the convection from small platinum wires (Phys. Rev., l. c.) have shown that the value of B calculated from measurements on wires ranging from 0.004 to 0.050 cm. in diameter is equal to 0.43 cm. and is entirely independent of the diameter, and of the temperature of the wire.

This result gives practically perfect agreement when tested by Kennelly's data on the convection from copper wires ranging from 0.01 to 0.07 cm. diameter.

Experimentally, therefore, for wires from 0.004 to 0.070 cm. diameter, the above theory has been proved to give the correct relation between power consumption and the diameter. In order to determine whether the theory is generally applicable, it was decided to make measurements of the convection losses from plane surfaces. In this case a new difficulty is encountered—the fact that radiation is often much greater than convection.

Convection from Plane Surfaces.

These experiments were made by measuring the temperature of metal disks 7½ inches in diameter and ¼ inch thick when heated electrically by a known amount of power. The apparatus used is shown in Fig. 2. The metal disk B is provided with a flat heating unit D of calorite, placed between mica plates and held in place below the plate by a thin sheet of calorite. The platinum : platinum-rhodium thermocouple A is attached to the under side of the plate by a small screw, so that the junction is tightly clamped to it.

The large cast iron cylinder F, 9⅝ inch (24 cm.) in diameter and 5 inches (12.5 cm.) high, served to hold the heat insulating material G in place and thus to prevent as much as possible the

loss of heat from the plate except from the single exposed surface. The plate *B* was held in place by the steel rods *E* (⅛ inch (0.3 cm.) diameter). Mica rings *C* were used to keep the insulation from escaping from the cylinder when it was turned on its side or inverted.

The apparatus was so designed that the loss of heat from the plate to the cylinder would be as small as possible. To find exactly what this loss of heat was, so that correction could be made for it, a sheet iron cylinder of 9½ inches (24 cm.) diameter and 5 inches (12.5 cm.) depth was placed on the one shown in the figure, and this was filled with insulation and the metal disk

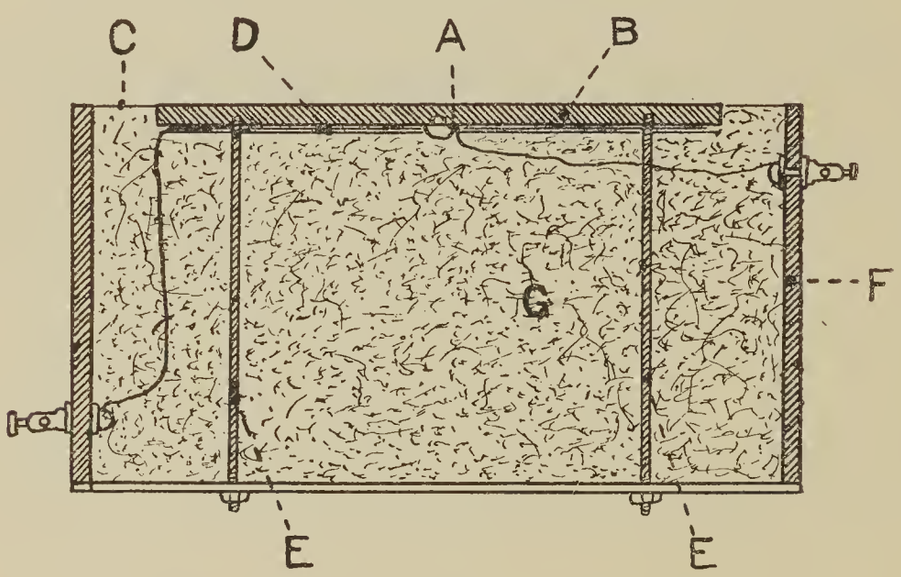


FIG. 2.

Cross Section of Apparatus for Determining Heat Losses from Metal Disks.

heated to various temperatures. From measurements of the specific thermal resistance of this material the heat loss thru the upper part could be calculated sufficiently accurately, and by deducting this from the total watts actually observed, with insulation above as well as below the plate, the amount of heat lost thru the metal rods *E*, mica ring *C* and insulation *G* could be accurately determined. This quantity was applied, in measurements on convection, as a correction to the total watts, in order to find the watts lost by convection and radiation from the upper surface of the plate. This correction was relatively small, amounting in most cases to only about 6 to 8 percent.

The thermocouple wires, being placed below the unit and embedded in the insulation, would reach the temperature of the surface itself. The heat conductivity of all metals is so good that with the amounts of heat flux employed in these experiments the drop in temperature from one side of the plate to the other could never have exceeded 7°, and must usually have been much less than this.

The tests conducted with this apparatus, as well as the building of the apparatus itself, have been carried out under the direction of Mr. C. P. Randolph, at the Heating Device Research Laboratory at Great Barrington.

The experiments have thus far included measurements of the total heat losses from metal disks of the following materials:

1. Copper, oxidized by heating to a red heat.

2. Copper, calorized (that is, surface impregnated with aluminum).

3. Silver, pure, polished.

4. Cast iron, fresh machined surface.

5. Cast iron, oxidized by heating to a red heat.

6. Aluminum paint (on cast iron).

7. Gold enamel on cast iron.

8. Monel metal, bright.

9. Monel metal, oxidized by heating to red heat.

The measurements were made by heating the disk with a given current at constant voltage and waiting until a stationary temperature had been reached, the wattage being recorded. Then the current would be raised to a value which would raise the temperature about 100°, and another reading taken. At lower temperatures the readings were usually taken every 40° to 50°. These results were plotted and a smooth curve drawn thru the points. Usually all the points fell very close to the line. The results taken from these curves are recorded in Table VI.

Table VI.

Total Heat Loss from Various Surfaces in Quiet Air. Surfaces vertical unless otherwise indicated.

Room Temperature 300 °K. In Watts per Square Cm.

	Surface	325°K	350°K	400°K	500°K	600°K	700°K	800°K	900°K
1	Copper, oxidized	0.025	0.054	0.142	0.370	0.730	1.35	2.7	.....
2	Copper, calorized	0.018	0.037	0.090	0.233	0.420	0.68	0.99	.....
3a	Silver, pure, vertical	0.011	0.028	0.065	0.156	0.260	0.385	0.530	0.670
3b	Silver, horizontal, upper surface exposed	0.012	0.029	0.071	0.168	0.284	0.420	0.57	0.74
3c	Silver, horizontal, lower surface exposed	0.006	0.015	0.036	0.081	0.136	0.201	0.292	0.405
4	Cast Iron, bright	0.014	0.034	0.087	.....	.....	.....	.....	.....
5	Cast Iron, oxidized	0.020	0.053	0.130	0.357	0.713	1.19	1.71	2.16
6	Aluminum paint	0.023	0.050	0.110	.....	.....	.....	.....	.....
7	Gold Enamel	0.017	0.042	0.101	.....	.....	.....	.....	.....
8	Monel Metal, bright	0.020	0.048	0.102	.....	.....	.....	.....	.....
9	Monel Metal, oxidized	0.020	0.050	0.114	0.280	0.530	0.92	1.36	1.86
10	Radiation black body	0.018	0.040	0.104	0.322	0.717	1.37	2.37	3.82
11	Radiation, silver	0.0003	0.0008	0.0022	0.0087	0.023	0.048	0.083	0.134
12	Convection silver, vertical surface	0.011	0.026	0.063	0.147	0.237	0.337	0.447	0.536
13	$\varphi_2 - \varphi_1$	0.00647	0.013	0.028	0.064	0.104	0.151	0.200	0.259
14	B, Film thickness, cm.	0.58	0.50	0.44	0.44	0.44	0.45	0.45	0.48
15	Calculated convection, (B = 0.45 cm.)	0.014	0.029	0.062	0.142	0.231	0.335	0.444	0.575
16	B, for horizontal surface exposed above, cm.	0.54	0.46	0.41	0.41	0.40	0.41	0.41	0.42
17	B, for horizontal surface exposed below, cm.	1.08	0.93	0.82	0.89	0.92	0.99	0.96	0.96
18	Calculated convection (Lorenz)	0.0114	0.0270	0.0642	0.154	0.254	0.368	0.485	0.607
19	Ratio, percent	104	104	102	105	107	109	108	113

It will be observed that the difference between the losses for the vertical position and for the horizontal position with the upper surface exposed is relatively very slight. This fact is strong evidence that the phenomenon of heat convection is much simpler than has usually been supposed.

The amount of heat radiated from the silver surface can be calculated fairly accurately from Hagen & Ruben's formula (Ann. Phys, **8**, 1 (1902)), which gives the emissivity of any metal for long wave lengths in terms of the electrical resistivity of the metal. This formula has been amply verified for many

metals up to wave lengths of about 4 microns. For shorter wave lengths it ceases to hold accurately. The formula

$$E = 0.365 \sqrt{\frac{\sigma}{\lambda}} \tag{25}$$

where σ = specific electrical resistivity in ohm-cm.

λ = wave length of the radiant energy in cm.

For silver $\sigma = 1.76 \times 10^{-6}$, at 300° K.

Now, according to Wien's displacement law the wave length of the radiant energy of maximum intensity from a black body is

$$\lambda_M = \frac{0.29}{T} \; cm. \tag{26}$$

For temperatures up to about 700° most of the energy in the spectrum is of wave length greater than 2 microns, and therefore up to this temperature we should expect Hagen and Ruben's formula to hold.

Since for pure metals σ increases about proportional to the absolute temperature, and from Wien's law λ is inversely proportional to T, it follows that E itself, up to about 700°, would be proportional to T. At 300° K. (about room temperature), λ_M is 0.00096 cm., whence $E = 0.0156$.

That is, at 300° silver would radiate only 1.6 percent as much as a black body. Up to about 700° this would increase approximately proportional to the temperature, but above that probably more slowly. According to Kohlrausch's Tables, even for a wave length of 1.00 micron, a shorter wave length than would be radiated from silver below its melting point, the reflectivity is still 96.5 percent, therefore the emissivity is only 3.5 percent.

The remarkably small amount of radiation from the silver surface was very strikingly apparent during the experiments. Even when the silver plate was heated to 700° C. the hand could be held within an inch of it with perfect comfort, whereas with any of the other surfaces at this temperature the amount of heat radiated made it impossible to hold the hand near it for more than a couple of seconds.

Another interesting and significant observation made during the experiments was that the air near the plates, even when these were heated to redness, was only heated to a distance of less

than a quarter of an inch from the plates. For example, a piece of paper would not begin to char until it was brought within about $\frac{3}{16}$ of an inch of the plate. With the plates at a lower temperature, say 250°, the same could be observed by bringing the back of a finger near the plate. Until within about a quarter of an inch practically no heat but the radiant heat was felt. The finger could not comfortably be brought closer than that distance. This is one of many simple demonstrations of the existence of a film of heated gas of about 4 to 5 mm. thickness.

Returning now to the consideration of the radiation from the silver plate, it should be pointed out that when this plate was heated above about 400° C. it lost its high polish and reflected only diffusely, but remained very white. This change, however, did not materially alter its radiating properties, for upon cooling after heating to about 700° C. the power consumption at 200° and 300° C. was practically identical with that previously determined.

We may therefore safely conclude that the values we have calculated for the radiation from silver may be applied accurately to the piece of silver used in these experiments. In this way we calculate the energy radiated from the silver at the various temperatures.

These results, together with the energy radiated from a black body (calculated from equation (2)), are given in the 11th and 10th lines of Table VI.

By subtracting the radiated energy from the total we obtain the energy lost by convection. This is given in line 12.

We are now in position to calculate the film thickness B for convection from a plane surface. According to equation (11) we find B from

$$B = \frac{\varphi_2 - \varphi_1}{\mathbf{W}_c} \tag{27}$$

In line 13 are given the values of $\varphi_2 - \varphi_1$ taken from Table V, and in line 14 the values of B calculated from them. The mean of these values of B is 0.45 cm. Taking this value and calculating $\mathbf{W}_c$ from equation (11) we get the figures of line 15.

The agreement with the observed convection given in line 12 is very satisfactory.

The value of B, 0.45 cm., obtained from these experiments is in

remarkably good agreement with the value 0.43 cm. obtained as an average from many experiments with small wires. This fact is perhaps the strongest indication of the usefulness and probable correctness of the present "conduction theory" of convection.

Of course the gap between wires of 0.7 mm. diam. and plane

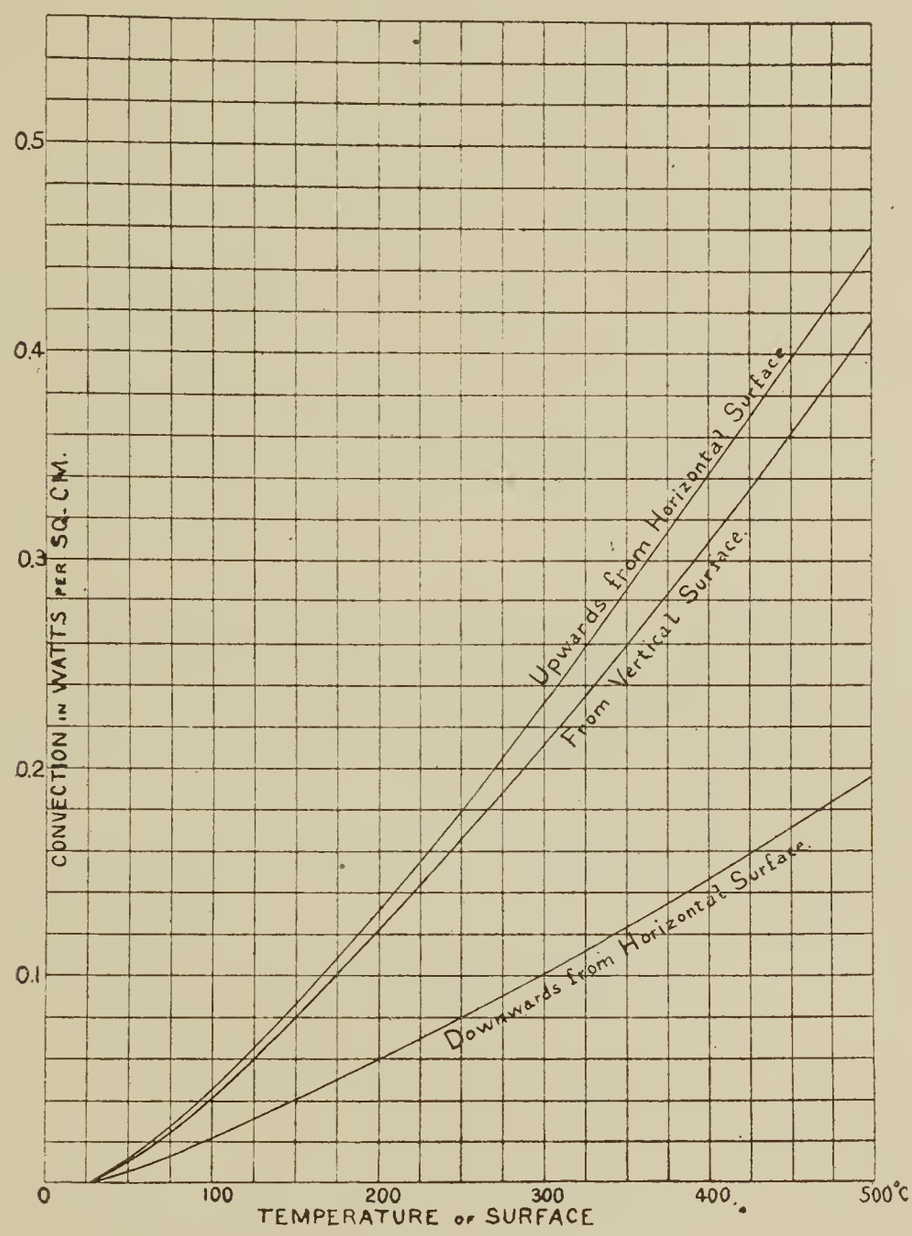


FIG. 3.
Convection from Plane Surfaces.

surfaces 19.0 cm. in diam. is very large, still it would seem that the fact that the theory enables us to calculate the convection for these two extremes is sufficient to warrant its application to spheres and cylinders of any size. Actual experiments on the heat losses from a silver rod 6.0 mm. in diameter are in progress, and seem to indicate the substantial correctness of the theory.

The convection upwards from a horizontal surface is slightly greater than from a vertical surface. The values of B at various temperatures for this case are given in line 16. The mean value of B from 400° to 900° is 0.41 cm. Thus the convection upwards from a plane surface is about 12 percent greater than from a vertical surface. The convection downwards from a horizontal surface gives for a mean $B = 0.92$ cm. Therefore the convection downwards is about one-half as great as that upwards.

Of course in this case there is in no sense free convection, for there is a layer of stagnant air below the plate which is limited in thickness only by the rate at which it gradually pours off upwards from the edges. We find that by wrapping a piece of asbestos paper around the iron cylinder (in inverted position, see Fig. 2) so that its edge extends about 1 inch below the level of the plate, that the amount of heat lost by convection is reduced to a small fraction of what it is without the asbestos paper.

A plot of the losses by convection from surfaces in the three positions is given in Fig. 3. These results are obtained from the data on lines 3a, 3b and 3c of Table VI by substracting the radiation given in line 11. For convenience the temperature is given on the centigrade scale.

At temperatures from 400° K. upwards the values of B show no distinct temperature coefficient. We may safely conclude, just as we were able to do with the convection from small wires, that the thickness B of the film is independent of the temperature of the plate (or wire).

It seems very remarkable that this is so, and as yet no satisfactory explanation has been found.

At temperatures less than 50° above room temperature the experiments indicate that the convection is somewhat less than would be calculated from the theory. Thus we find that at a temperature only 25° above room temperature the value of B is 0.58 instead of 0.45. In other words, the convection is only about 80 percent of that calculated. There are good theoretical reasons for believing that, for extremely small differences of temperature B would increase indefinitely, or, in other words, there would be no convection, but only conduction.

For very small temperature differences probably some such

relation as that calculated by L. Lorenz (Ann. Phys. **13**, 582 (1881)) holds. Lorenz, by making certain reasonable assumptions, calculated theoretically the convection from large vertical plane surfaces. He obtained the formula:

$$\mathbf{W_c} = 0.548 \sqrt[4]{\frac{\mathbf{c}\, g\, \mathbf{k}^3}{\mathbf{h}\, H\, T}} \sqrt{\mathbf{d}}\, (T_2 - T_1)^{5/4} \qquad (28)$$

where

$\mathbf{c}$ = specific heat of the gas
$\mathbf{k}$ = its heat conductivity
$\mathbf{h}$ = its viscosity
T = its temperature
$\mathbf{d}$ = its density
g = gravitational constant
T_2 = temperature of the plane surface
T_1 = temperature of the gas at a great distance from the plane
H = height of the plane.

From the assumptions made by Lorenz we should expect this equation to hold accurately only for small temperature differences.

In its form the equation agrees well with Dulong and Petit's equation for convection. Lorenz finds the exponent 5/4, whereas Dulong and Petit found empirically 1.233.

To determine the numerical factors for air at 300° K. we will substitute the values

$\mathbf{c}$ =	0.72	joules per gram per °C.
$\mathbf{k}$ =	0.000250	watts per cm. per °C.
$\mathbf{h}$ =	0.000182	grams per sec. per cm.
$\mathbf{d}$ =	0.00117	grams per sec.
g =	981	cm. per sec.^{2}

The equation thus becomes (for air at 27° C.):

$$\mathbf{W_c} = .000399\, H^{-1/4}\, (T_2 - T_1)^{5/4} \qquad (29)$$

If we take H = 15 cm., corresponding roughly to a disk 7.5 inches in diameter, we have:

$$\mathbf{W_c} = .000203\, (T_2 - T_1)^{5/4} \qquad (30)$$

The convection at various temperatures has been calculated from this equation, and is given in line 18, Table VI. On line 19

is the ratio of the results of line 18 to the observed convection given on line 12. The results are a little too high, but by taking the coefficient in the last equation 0.000195 instead of 0.000203 the agreement up to 700° would be excellent.

It is surprising that this equation should hold up to such high temperatures when the heat conductivity, viscosity and density all vary so rapidly with the temperature, and none of these variations were taken into account in deriving the equation.

The observed convection losses given on line 12, Table VI, were plotted on logarithmic paper and were found to be very nearly straight, only a slight curvature above 600° being observable. The average slope of the curve up to 600° is 1.24, which means that the convection increases proportionally to the 1.24 power of the temperature difference.

Thus we see that Lorenz's and Dulong and Petit's laws in regard to the relation between temperature and convection hold quite accurately even up to very high temperatures.

However, at high temperatures it must be only a coincidence that Lorenz's law gives results agreeing so closely with those calculated from φ on the assumption of constant film thickness. By plotting the data on convection from platinum wires in air (Phys. Rev., *l. c.*) at very high temperatures it is found that the exponent b of Dulong and Petit's equation increases from 1.24 at low temperatures up to 1.53 at 1700° K. Similar increases are observed with other gases: nitrogen, carbon dioxide and hydrogen. Especially with carbon dioxide this increase is very marked, the exponent increasing from about 1.30 at low temperatures up to 1.72 at 1700° K. This fits in with the fact that Sutherland's constant C (see Table IV) is 260 for carbon dioxide, being much higher than for the other gases.

Radiation from Plane Surfaces.

Having now determined the amount of heat carried away from plane surfaces by convection, we are prepared to estimate the energy losses by radiation from each of the surfaces studied.

If we subtract from the total energy losses given in Table VI (lines 1 to 9) the energy lost by convection (line 12) we obtain the energy radiated. If we now divide these results by the calculated radiation from a black body (line 10) we obtain the

emissivity E of the surface. Table VII contains the results calculated in this way. The emissivity E is expressed as percentage radiation, taking the radiation from a black body as 100 percent.

TABLE VII.

Emissivity of Various Surfaces.
Giving Radiation as Percentage of that from a Black Body.

Room Temperature 300 °K. Temperature °K.

	Surface	325	350	400	500	600	700	800	900	Mean
1	Copper, oxidized	77	70	76	69	69	74	73	. .	72
2	Copper, calorized	39	28	26	27	26	25	23	. .	26
3	Silver (calculated)	1.7	1.9	2.1	2.7	3.2	3.5	3.5	3.5	3.0
4	Cast Iron, bright	17	20	23	. .	. .		. .	. .	22
5	Cast Iron, oxidized	50	67	64	65	67	62	53	42	62
6	Aluminum, paint	67	60	45		. .	. .	. .	. .	50
7	Gold, enamel	33	40	37	. .	. .	. .	. .	. .	37
8	Monel Metal, bright . . .	50	55	38	. .	. .	. .	. .	. .	43
9	Monel Metal, oxidized . .	50	60	49	41	41	42	38	35	43

Theoretically the emissivity E should be a function of the temperature. In most cases the total energy emissivity increases with the temperature principally because the energy of maximum intensity shifts into a part of the spectrum where the emissivity is greater. But in some cases the opposite might be true.

Nevertheless, as an approximation we may assume that the emissivity is constant, and in calculating the total losses from plane surfaces we may simply add the calculated convection (line 15, Table VI) to the product of the mean emissivity and the radiation from a black body. The results for total energy losses have been calculated in this way, and are plotted in Fig. 4.

The most serious criticism that can be raised against the above work on convection losses from surfaces is the fact that we have calculated the radiation from the silver surface. There is, of course, a possibility that, owing to some unforeseen change in surface condition, the silver may actually have radiated more than the calculations give. The fact that the emissivities found on the basis of these calculations show no distinct temperature trend is strong evidence that no large error has been made in this way. However, to remove this uncertainty we have started

experiments to measure directly the relative amounts of radiation from various surfaces, and will probably publish these results at a later date.

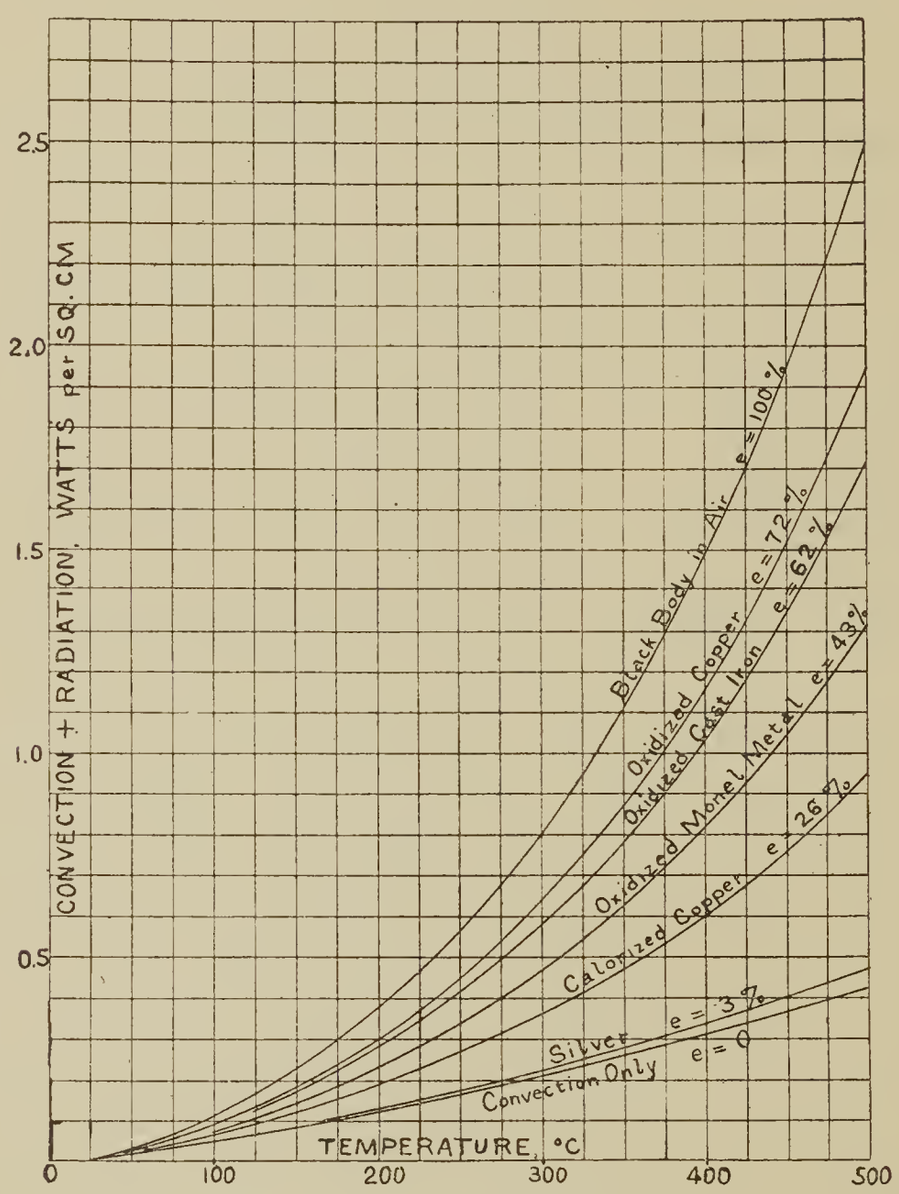


FIG. 4.
Total Losses from Heated Surfaces in Air.

Effect of Air Currents on Convection.

In a previous paper (Proc. A. I. E. E., *l. c.*) Kennelly's data on forced convection from small copper wires were analyzed in the light of the present theory. The calculated film thickness was very much less than in quiet air. For example, for a wire heated 211° above room temperature the values of B for various wind velocities were:

Wind Velocity Cm. per Second	B. (Cm.)
330	0.0162
900	0.0077
1,800	0.0044

In quiet air B was found to be 0.43 cm.

For wires from 0.01 to 0.02 cm. in diameter the size of the wire had no effect on the value of B calculated from the observations, and it was thought that probably the film thickness B found from experiments on plane surfaces would yield similar results.

Altho only very rough experiments have been made to test this point, yet they prove that the values of B obtained from experiments on plane surfaces are from 5 to 7 times larger than those calculated from wires.

This result was obtained simply by taking measurements of the power necessary to maintain a 7½-inch disk of calorized steel at a temperature of 500° C., when subjected to the wind produced by an electric fan. The wind velocities were measured by a calibrated anemometer. The experiment gave the results in Table VIII.

TABLE VIII.

Effect of Air Currents on Convection from a Plane Surface.

Temperature of surface 500 °C. $\varphi_2 - \varphi_1 = 0.189$

Wind Velocity Cm. per Sec.	Total Energy Watts /Cm²	Convection Watts /Cm²	B Obs. Cm.	B Cal. Cm.
0	1.42	0.41	0.44	0.45
270	2.17	1.16	0.155	0.152
370	2.37	1.36	0.131	0.132
410	2.45	1.44	0.124	0.126

A formula which agrees sufficiently well (see last column) with these results is:

$$B = 0.45 \sqrt{\frac{35}{35 + V}} \qquad (31)$$

where V is the wind velocity in cm. per sec.

If we calculate B by the formulas deduced from Kennelly's data we would have 0.025, 0.019 and 0.018, instead of the 0.155, 0.131 and 0.124 given in next to the last column of Table VIII.

Carpenter (Heating and Ventilating Buildings, Wiley & Sons,

1903) gives the following data on the heat loss from a 2-inch steam pipe at 66° above room temperature.

TABLE IX.

Velocity of Air Ft. per Second	Heat Loss *BTU* per Sq. Ft. per °F per Hour
9.8	6.3
4.1	4.3
6.7	5.5
5.5	5.5

Converting these to metric units we have:

TABLE X.

Wind Velocity Cm. per Sec.	Total Heat Loss Watts per Cm² per °C	Convection Watts per Cm² per °C	*B* Cm.
300	.0036	.0031	.084
126	.0024	.0019	.137
205	.0031	.0026	.100
168	.0031	.0026	.100

To calculate the convection it was assumed that the radiation was equal to that from oxidized cast iron, that is, to 65 percent of that from a black body. This gives 0.00052 watts per cm.² per °C. for the radiation.

For the calculation of B the value of $\varphi_2 - \varphi_1$ for one degree difference of temperature was taken as 0.00026.

These results give values of B somewhat lower than those of our experiments. This is probably due principally to the smaller surface employed. For forced convection undoubtedly the extent of the surface plays a larger part than in the case of free convection.

The effect of air currents can probably best be taken into account by calculating the convection for quiet air and then multiplying by a factor which depends on the wind velocity only. For plane surfaces this factor would be:

$$\sqrt{\frac{V + 35}{35}}$$

Kennelly had found for the convection from small wires that the effect of wind velocity can be allowed for by multiplying by $\sqrt{\frac{V + 25}{25}}$. These two factors are so nearly the same that it is evident that the method would give good results for both plane surfaces and wires.

It seems, therefore, that for forced convection the film theory loses its usefulness. It is probable that for cylinders or wires in strong air currents the formula deduced theoretically by A. Russell (*l. c.*) would be more generally applicable.

Russell's equation gives for the power loss by convection in any fluid:

$$\mathbf{W}_c = 8 \sqrt{\frac{\mathbf{c}\ \mathbf{d}\ \mathbf{k}\ Va}{\pi}}\ (T_2 - T_1)$$

where $\mathbf{W}_c$ = convection loss per unit of length
$\mathbf{c}$ = specific heat of the fluid
$\mathbf{d}$ = density of the fluid
$\mathbf{k}$ = heat conductivity
V = velocity
a = radius of the wire
T_2-T_1 = difference of temperature between the wire and the fluid.

This equation was calculated on the assumption that the fluid has no viscosity, is incompressible and has constant density and heat conductivity. Hence it should only give roughly approximate values when applied to the problems of cylinders being cooled by currents of air.

If this formula is tested out by Kennelly's data on forced convection it is found to give results too high. For the three wires tested the ratios between the observed and calculated values of $\mathbf{W}_c$ were:

Diameter of Wire — Cm.	Ratio : Observed — Cal.
0.0101	60 : 100
0.0159	65 : 100
0.0204	71 : 100

These ratios do not perceptibly vary, while the velocity changes from 200 to 1,800 cm. per sec., or the temperature difference changes from 50° to 300°, so that we may say that Russell's formula gives the correct relationship between convection and both temperature and velocity. The reason that the calculated convection is too high is probably the fact that it was necessary to neglect the effect of viscosity in deriving the formula. As the diameter of the cylinder increases we would expect the formula to become more accurate.

If we test out the formula by the data given in Table X on the forced convection from a 2-inch steam pipe we find:

Wind Velocity	Convection		Ratio
	Observed	Calculated	
300	0.0031	0.00352	0.88
126	0.0019	0.00228	0.84
205	0.0026	0.00290	0.89
168	0.0026	0.00263	0.99

We find that the Russell formula gives quite accurate results on large cylinders.

It is fairly safe to assume, therefore, that the formula

$$\mathbf{W}_c = \epsilon\,(T_2 - T_1)\sqrt{\frac{\mathbf{c\,d\,k}\,Va}{\pi}}$$

gives reasonably well the heat loss by convection from wires and cylinders in air at high velocities (300 cm. per sec. or more). Here ϵ is a number which depends on the diameter of the wire or cylinder, being about 7 or 8 for large cylinders, and about 5 or 6 for small wires (0.01 to 0.1 cm.).

For forced convection in air from a cylinder in the neighborhood of 100° above room temperature we have:

$\mathbf{c}$ = 0.73 joules per g. per °C.
$\mathbf{d}$ = 0.0010 g. per c.c.
$\mathbf{k}$ = 0.00028 watts per cm. per °C.

Whence

$$\mathbf{W}_c = 0.000255\,\epsilon\,(T_2 - T_1)\sqrt{Va} \text{ watts per cm.}$$

where ϵ = a number from 5 to 8, varying with the diameter as described above.

Effect of Temperature, Pressure and Nature of the Gas upon Convection.

An extensive series of experiments have been carried out to measure the free convection from horizontal platinum wires in large volumes of various gases (air, hydrogen, carbon dioxide). In the experiments in air the pressure was varied from 1.0 cm. to atmospheric pressure, while the temperature of the surrounding gas was maintained at each of the following temperatures: 25° C., 250° C., 500° C., 600° C. At each pressure the temperature of the wire was varied from 100° C. up to about 1400° C. In another experiment the convection from a hot platinum wire in air at a temperature of —185° C. was measured.

These results will probably be published in the near future, but the following preliminary statement may now be made:

The thickness B of the plane film varies roughly inversely proportional to the density of the gas. Whether the changes in density are due to changes in temperature, or in pressure, or even to the substitution of a gas of different chemical composition, seems to have little effect on the validity of this rule.

Summary and Conclusions.

1. The total energy loss from a heated surface in a gas consists of two parts, convection and radiation.

2. If the emissivity of the surface is known the radiation can be calculated from the Stefan-Boltzman law.

$$\mathbf{W_R} = 5.90\ E \left[\left(\frac{T_2}{1000} \right)^4 - \left(\frac{T_1}{1000} \right)^4 \right] \text{ watts per cm.}^2 \quad (3)$$

E is the emissivity of the surface, and varies for different surfaces from 0 to 1. For any one surface it is accurate enough for most purposes to consider it independent of the temperature.

3. Free convection from a surface consists essentially in conduction thru a film of gas of definite thickness, and can be calculated by the ordinary laws of heat conduction when the film thickness is known.

4. The loss by convection is equal to the product of two factors, thus:

$$W_c = S\ (\varphi_2 - \varphi_1) \quad (9)$$

S is the shape factor, and depends only on the shape of the body and on a quantity B, a constant for any given gas under given conditions of temperature and pressure. B is equal to the thickness of the film of relatively stationary gas thru which conduction takes place in the case of convection from a plane surface. $\varphi_2 - \varphi_1$ is equal to $\int_{T_1}^{T_2} \mathbf{k}\, dT$ where $\mathbf{k}$ is the heat conductivity of the gas. The heat conductivity can be readily calculated from the specific heat and viscosity of the gas. Tables of φ for air, nitrogen, hydrogen, carbon dioxide and mercury vapor are given. A curve of φ as a function of the temperature is given for air.

5. The shape factor S has been calculated for the case of convection from planes, cylinders and spheres.

In this way the following formulas for convection are derived:

For Plane Surfaces:

$$\mathbf{W_c} = \frac{\varphi_2 - \varphi_1}{B} \text{ watts per sq. cm.} \tag{11}$$

For Horizontal Cylinders of Diameter a:

$$\mathbf{W_c} = \mathbf{S}\ (\varphi_2 - \varphi_1) \text{ watts per cm.} \tag{17}$$

where $\mathbf{S}$ is found from the equation:

$$\frac{a}{B} = \frac{\mathbf{S}}{\pi}\, e^{-\frac{2\pi}{\mathbf{S}}} \tag{16}$$

A table (Table III) of $\mathbf{S}$ as a function of $\frac{a}{B}$ is given. If a curve is prepared from this data the value of $\mathbf{S}$ may be found in any particular case with great ease.

For Spheres of Diameter a:

$$W = S\ (\varphi_2 - \varphi_1) \text{ watts} \tag{23}$$

where S is found from the equation:

$$\frac{1}{a} - \sqrt{\frac{\pi}{S\ B}} = \frac{2\pi}{S} \tag{21}$$

In each of these cases the convection can be calculated if we know $\varphi_2 - \varphi_1$ and B the film thickness for a plane surface.

7. For air at atmospheric pressure and room temperature, experiments on wires of various sizes and on plane surfaces give

B independent of the temperature of the heated body. The experiments on wires gave

$$B = 0.43 \ cm.$$

and the experiments on vertical plane disks gave

$$B = 0.45 \ cm.$$

8. From horizontal plane surfaces the convection from the upper surface is about 10 percent greater than from a vertical surface, but from the lower surface about 50 percent less than from the vertical surface.

9. The emissivity of various surfaces was found to be in percent:

Black body	100
Copper, oxidized	72
Copper, calorized	26
Silver	3
Cast iron, bright	22
Cast iron, oxidized	62
Aluminum paint	50
Gold enamel	37
Monel metal, bright	43
Monel metal, oxidized	43

The total losses from these surfaces at various temperatures up to 600° C. are given in Table VI. In the curves of Fig. 4 are given plots of the total energy losses calculated by adding the radiation (from Stefan-Boltzman law) and convection (from $(\varphi_2 - \varphi_1)/B$).

10. Dulong and Petit's law and Lorenz's law for the relation between convection and temperature of the hot body hold very satisfactorily up to fairly high temperatures. At low temperatures these equations probably give the convection even more accurately than those calculated from the film theory, but at high temperatures the film theory gives much better results. Furthermore, the newer theory enables the effect of the shape and size of the body to be taken into account.

11. For forced convection, that is, loss of heat in strong air currents, the film theory does not seem to apply. On the other

hand, an equation derived by A. Russell seems to agree well with the experimental data available.

12. For other gases than air, or for air at other temperatures or pressures, the value of B can be assumed to be inversely proportional to the density of the gas. This will give results usually accurate enough for the calculation of convection from small wires.

Research Laboratory,
General Electric Co.,
Schenectady, N. Y.
Aug. 26, 1912.

DISCUSSION.

Dr. W. Lash Miller: Before asking for discussion I should like to emphasize the great simplification that Dr. Langmuir has introduced by his assumption that around each surface there is a small volume of gas through which heat passes mainly by conduction. Those familiar with the theory of diffusion know that there is almost perfect analogy between heat conduction and diffusion; in this analogy Dr. Langmuir's assumption of an adherent layer of gas corresponds to Noyes and Whitney's theory of the liquid film. It would be difficult to name a paper published in the last fifteen years that has had more important practical consequences than that by Noyes and Whitney; and as Dr. Langmuir's experimental work shows that his assumption is justified, we may well look forward to a similar rapid advance in the practical applications of the theory of conduction of heat.

Dr. Carl Hering: The discussion of that film is very interesting, but there is an analogy in the opposite case to the one discussed here, namely, when the body receives the heat. It is well known, and I have cited it before this Society, that you can paste a postage stamp on the fire side of a boiler tube and it will not char. This shows there is a film around the outside of the boiler tube in which the temperature gradient must be something enormous, that is to say, the resistance of it must be very great.

I tried a very crude experiment one time, of pasting several postage stamps one over the other, and as nearly as I remember, when I got to the third or fourth thickness the outside one began to char, which was a very crude measurement of the thickness of that film. I think it was about 1/100 of an inch, or something like that.

The question of the loss of heat from a surface is quite important to furnace men, as it may be possible to make that surface resistance so high that the wall resistance may be made comparatively small. In other words, it may not be necessary to put very thick walls around our furnaces if we can so treat the outside of a furnace that the chief resistance or insulation is in this film. That would mean very much smaller furnaces.

I am very glad Mr. Langmuir took up that question of the old formula which I gave before this Society for cubical walls. I fully realized at the time that I stated it that it was not rigorous, but it is a little better than what we had before.

The curves in Fig. 4 seem to indicate that at very high temperatures the loss of heat from surfaces, say of molten metals, is very different with different materials—I had rather supposed that at high temperatures it did not make much difference what the metals were, that they would all lose about the same amount of heat per square foot of surface, but it seems from these curves that the loss will be very different, depending on what metal you are melting.

Dr. W. R. Whitney: I want to correct the impression which may have been given by Dr. Miller's remarks that the work which Noyes and I did, to which he referred, had a bearing on the discoveries of Dr. Langmuir. This work of Dr. Langmuir's is new and is what the Germans call *bahn brechend*. I have the greatest admiration and appreciation for this kind of work.

Prof. Jos. W. Richards: I hope that our members will take these lessons to heart, and try to diminish the heat losses in furnaces by varying the outside nature of the radiating surface. In a furnace proposition with which I was familiar some time ago I came to the conclusion that if they could so regulate their furnaces on the outside that they could keep them clean and light colored they would have a much smaller heat loss. Some

are experimenting with the outside of furnaces, polishing, plating, or painting them in different ways, and I would call attention to the fact that as you thus diminish the heat loss from the outside, the outside surface temperature will go up, and the *higher* the outside surface temperature rises under these conditions the more heat you save. You will find that is correct.

Dr. Carl Hering: I think that statement needs some modification, because if we imagine the furnace itself as made up of an infinitely thin shell, it will be the hottest, because it will be the temperature of the inside, and we all know that the charge will cool rapidly under those circumstances.

Prof. Jos. W. Richards: If the temperature of the outside is the same as the temperature of the inside there will be no loss of heat at all.

Dr. Irving Langmuir: I think Dr. Hering overestimates the resistance of the air close to the surface of a hot body. Under ordinary conditions in quiet air the thickness of the film of relatively stationary air is about 4 or 5 mm.—very much greater than the 1/100 in. which Dr. Hering concluded to be the thickness of the film from his experiments with the postage stamps. This not only follows from theoretical considerations, but has been found by actual measurements. We have explored the region around hot wires and heated surfaces by very fine platinum wires used as resistance thermometers. The temperature gradient is not limited to a very thin film, but actually extends out several millimeters from the surface.

For different gases the film thickness varies greatly, roughly inversely proportional to the density of the gas. For hydrogen the film extends so far that we can practically say that the convection in hydrogen is negligible and that heat is carried only by conduction.

There is not a great deal to be gained by silver plating the outside of a well built furnace. The surface resistance may be approximately doubled, but in any practical case the thermal resistance of the walls themselves will be many times greater than the surface resistance, so that by doubling the latter we will save only a relatively little of the total heat loss.

A paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 3, 1913, President W. Lash Miller in the Chair.

EXPERIMENTS WITH FURNACE ELECTRODES

By F. A. J. FitzGerald and A. T. Hinckley.

INTRODUCTION.

In the early history of the electric furnace the most serious objection raised by critics was the relatively high cost of the heat energy generated by the electric current as compared with that derived from fuel. While this criticism is a just one in many cases, it has not proved to be at all as serious as other criticisms which might have been made and which were not. One of these was the electrode problem. As long as furnaces were small there was little difficulty in obtaining satisfactory electrodes, but as furnaces rapidly increased in size the manufacture of suitable electrodes by no means kept pace with them. The methods of manufacturing electrodes for arc lamps or small carbon articles of that size are unsuitable for the production of the very large electrodes required for the modern furnace. The consequence was that when large furnaces came into commercial use the electrode question became a very serious one, for breakages continually occurred, and if these were avoided the large percentage of the electrodes lost in "butts" formed an important item in the total cost of running the furnace.

It was this serious problem which led a few large users of the electric furnace in Europe to undertake the production of electrodes for their own use. They were not hampered by a detailed knowledge of previous methods of manufacturing, and had not to overcome the unavoidable inertia of an established manufacturing process. It thus came about that the first very large electrodes that approached a satisfactory commercial article were probably produced by these manufacturers for their own use. Even the best, however, are crude in many respects, and can probably be greatly improved.

Some years ago the National Carbon Co. commenced a very extensive series of experiments for the purpose of finding the

best methods of making large carbons so as to obtain a thoroughly trustworthy electrode that would not fail under the severest usage and at the same time give the smallest wear under the particular conditions which surrounded its use. This study also involved the problem of joining electrodes together so as to avoid the loss in "butts." The object of this paper is to describe the methods used in testing the experimental electrodes and some of the results recently obtained.

LABORATORY TESTS.

Electrodes may be most readily compared in the laboratory by the determination of three physical properties: Real density, apparent density and electrical resistivity. These we call laboratory tests in order to distinguish them from the service tests which will be described later.

REAL DENSITY.

The real density, that is, the density of the material free from pores, may be considered as a measure of the chemical composition of the material, and increases as the amount of hydrogen in the hydrocarbons decreases. It is thus an indication of the relative rate of oxidation of the electrode, it being a general rule that hydrocarbons high in hydrogen are most readily oxidized.

The determination is made by grinding the sample to such a fineness that all pores are open to the liquid medium. For ordinary carbon electrodes particles passing through a screen having 100 meshes to the linear inch are sufficiently fine. Carbon ground to pass through a 200-mesh screen does not show any increase in the second decimal place in the density determination. The weighed sample is placed in a small specific gravity bottle with kerosene oil of known density, and evacuated to 5 mm. of mercury so that the pores are filled with the oil. The bottle is then filled with the oil, brought to a given temperature in a thermostat and weighed. The precision of the measurement is 0.5 percent.

APPARENT DENSITY.

The apparent density, *i. e.*, the density of the carbon including the pores, may be considered as a characteristic of the mechanical structure. It is influenced by every process through which the

carbon goes in the manufacture of the electrode, and is in general a measure of the relative rate of disintegration of the electrode in use. For large electrodes the most satisfactory method of determination is to weigh the whole electrode and calculate its volume from its dimensions. To secure a precision of 2 percent the weight and length should be measured to 1 percent and the diameter or periphery to 0.5 percent.

ELECTRICAL RESISTIVITY.

The electrical resistivity of carbon electrodes varies with both the real and apparent densities. Its determination is not necessary so much to show the physical properties of the carbon as to provide a means of comparison in electrical terms. With large electrodes its determination is made most readily by passing direct current through the whole carbon and measuring the potential drop through a known distance. For ordinary purposes it is sufficient to measure the resistivity to 0.0001 ohm, a precision of about 5 percent. This means, approximately, that the volts, amperes and length must be measured with a precision of 1 percent and the diameter or periphery with a precision of 0.5 percent. If these rules are followed the magnitude of the testing current is of no importance, provided that it is not sufficiently great to heat the carbon appreciably. Care must be taken in selecting the points for the potential contacts that the distance between them and the current contacts is so great that the equipotential surfaces are substantially plane surfaces at right angles to the axis of the electrode. The resistance of the potential contacts may be practically eliminated by drilling small mercury cups in the carbon or pressing the contact pins against the carbon at a pressure of about 3,000 pounds per square inch (210 kg. per square centimeter) when using a millivoltmeter having a resistance of 1.07 ohms.

SERVICE TEST.

Useful as the laboratory tests are on electrodes, they do not give sufficient information as to what may happen when the electrode is put in actual service. As was pointed out above, a serious objection to some of the earlier carbon electrodes used in electric furnaces was the large percentage which broke in service.

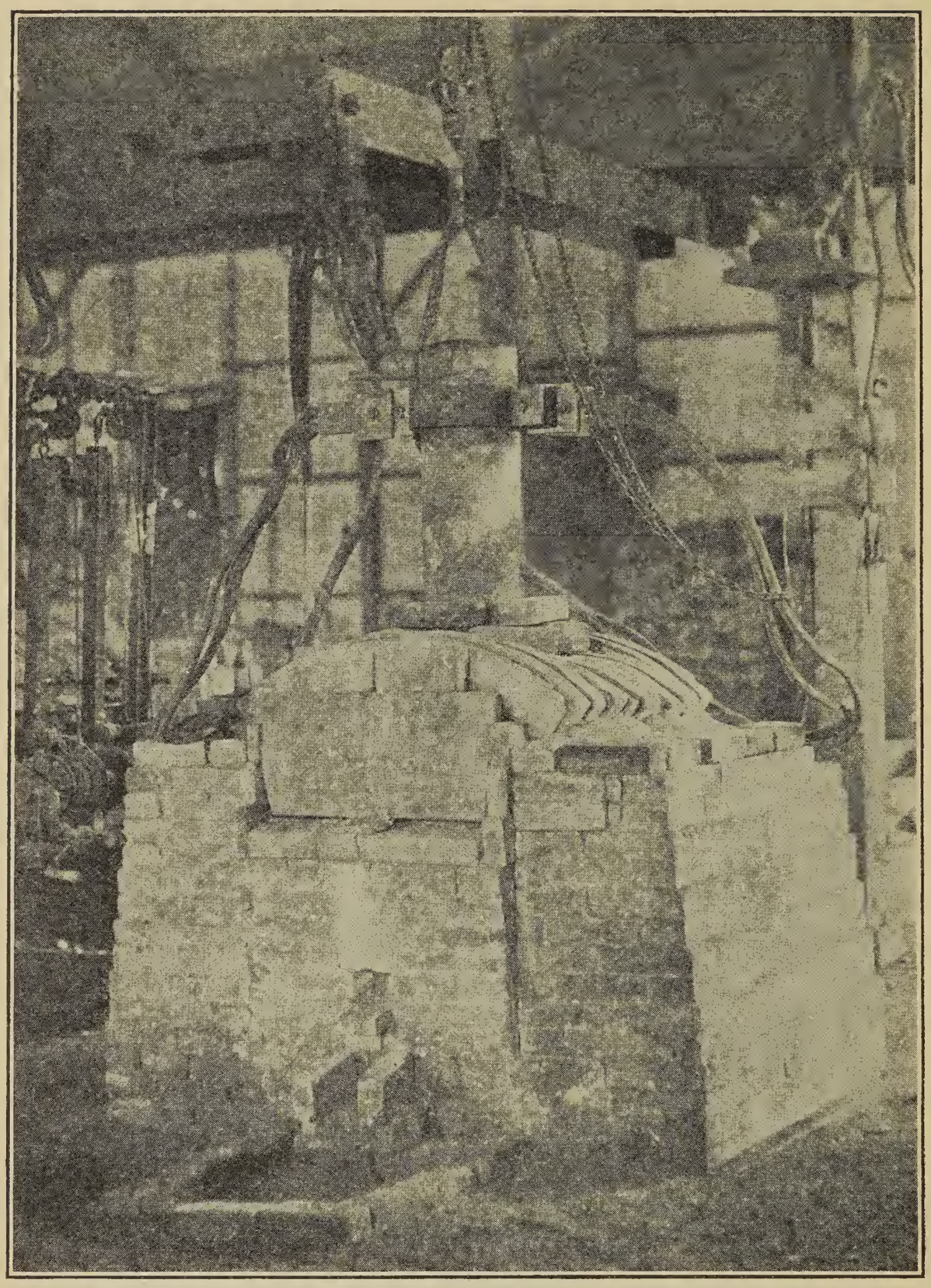


Fig. 1.

Another important consideration in furnace electrodes was the life, some electrodes giving apparently much longer service than others. It is not implied that the astonishing variation in the

figures for electrode consumption that is found in technical literature is due altogether to differences in the electrodes used, for this is in large part explained by the irrational method of estimating electrode consumption. For example, however useful from a purely commercial point of view the method of estimating electrode consumption in pounds per ton of steel may be, the important consideration when comparing electrodes is to determine how many kilowatt hours are generated in the furnace per unit weight of electrode. Studied from this point of view it is found that great variations exist.

In experimenting with the manufacture of carbon electrodes it is, therefore, necessary actually to use them in an electric furnace and thus test their behavior under working conditions.

Finally, in working on the problem of making electrodes which can be joined together, laboratory tests of the electrical resistance of the joint, or even tests of its mechanical strength, are not sufficient. It is necessary to use the jointed electrode in a furnace and determine just how it behaves throughout a series of runs.

THE FURNACE.

Probably the severest use to which an electrode can be put is in an open arc furnace where it works above a molten bath. Here the electrode is supported only by whatever method of suspension is employed, the part near the bath is heated to an extremely high temperature and is frequently exposed to cold air currents, and there are apt to be great surges of current which tend to cause sudden heating and thus severe strains. It was accordingly decided in these experiments to use a furnace of the Siemens type, shown in Fig. 1. The crucible in this furnace is 16 inches (405 mm.) deep, 17 inches (430 mm.) in diameter at the top and 15 inches (380 mm.) in diameter at the bottom. The bottom of the crucible was formed by tamping in a paste of ground carbon and tar, the current being carried to it by means of a carbon electrode 10 inches (254 mm.) square in section. In nearly all the experiments the electrodes used were 10 inches (254 mm.) in diameter and 60 inches (1,524 mm.) long.

In most tests the current used was at 50 volts, and the normal rate of generation was 150 kilowatts, though at times as much as 300 kilowatts were generated for periods lasting from 15 to 30

seconds, and occasionally the furnace was worked at 200 or 250 kilowatts for long periods.

In making a test the furnace was charged with cast iron and steel borings, and the electrode lowered until an arc was started. Then, if it was simply desired to find out if the electrode would stand severe usage without breaking, the current, which should

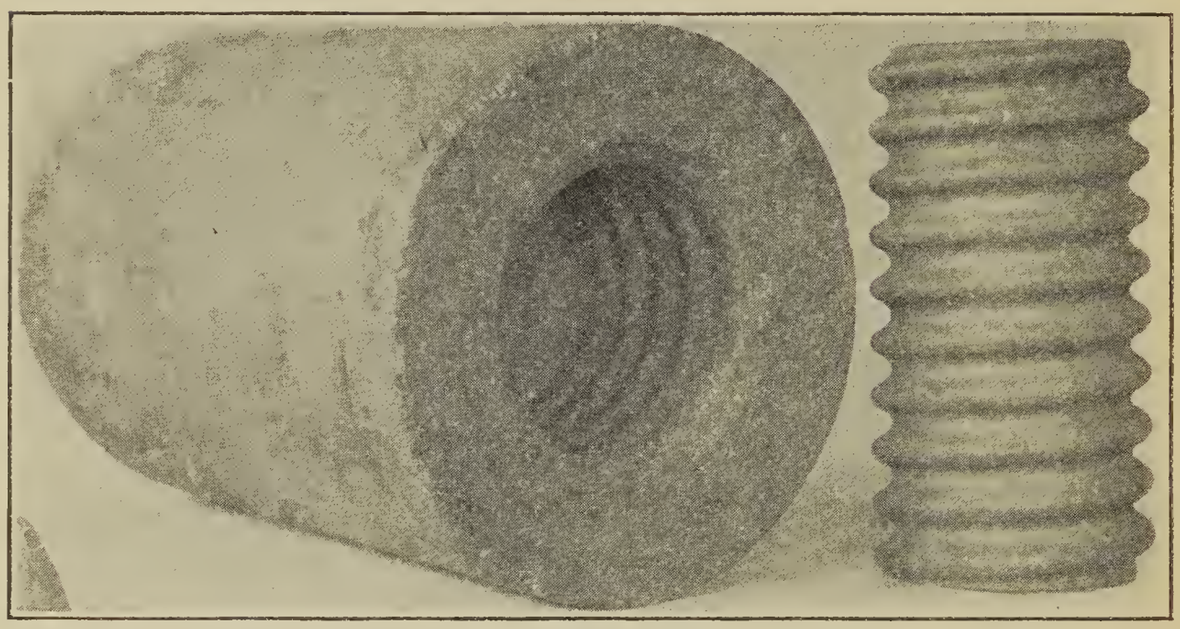


Fig. 2.

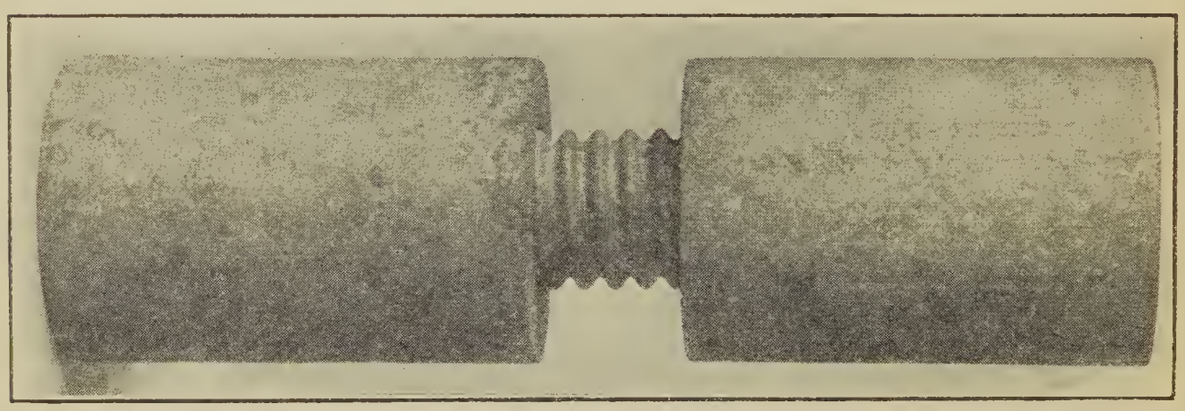


Fig. 3.

normally have been 150 kilowatts, was increased to 200 or 250 kilowatts. In general it is advisable to use an electrode, in a furnace of this sort, with a current density of not more than 40 amperes per square inch (6.2 amperes per sq. cm.), but occasionally higher current densities are necessary or desirable, so that the electrode must be constructed to stand these. Thus, in these experiments to determine the resistance under severe conditions,

current densities of 50 to 65 amperes per square inch (7.8 to 10.1 amperes per sq. cm.) were used. Moreover, for short periods the current density was as high as 77 amperes per square inch (11.9 amperes per sq. cm.).

In making tests of carbon consumption it was soon found that in order to get consistent results the furnace must always be run under identically similar conditions. Our assistants soon became very expert in carrying out this program, so that every heat lasted the same time, within a minute or two, and the total kilowatt hours were always the same. Before beginning a series of heats the electrode was carefully weighed. Then the furnace was charged with the cast iron and steel borings, these melted down and the furnace tapped. After a certain number of heats, usually eight, were run off the electrode was again weighed, and the total kilowatt hours used was divided by the loss in weight of the electrode, which gave the kilowatt hours per pound of electrode consumption.

JOINTED ELECTRODES.

As a result of numerous experiments it has been found that the joint best suited to the average furnace needs is made by using a cylindrical threaded plug, which is screwed equal distances into the ends of the two electrodes to be joined. A shallow rounded thread proves better than a pointed one, or even a truncated one, as there is less tendency to breakage during assembling. A specially prepared paste is used to insure good electrical contact, but this does not interfere in any way with unscrewing the joint when it is desired to replace a section. Fig. 2 is from a photograph of a section of electrode and the connecting plug. Fig. 3 shows the method of connecting two sections together.

TESTING JOINTED ELECTRODES.

In order to determine the resistance of the jointed electrode to severe usage the method followed was just the same as in the case of the ordinary electrode as regards overloading; but in addition to this a long series of heats were made so that the behavior of the joint as it finally worked down to the bath could be noted.

A very important consideration in the case of jointed electrodes

is the resistance of the joint. A joint might be made up, the resistance measured by ordinary laboratory methods and very good results be obtained, but when subjected to actual service the contact might easily become poor and a serious loss of energy occur. In order to determine this point the method illustrated by the diagram of Fig. 4 was used. *M* and *N* are two sections joined at *J*. Holes are drilled in these sections for the insertion of small graphitized carbon rods *1*, *2* and *3*, and these may be connected by means of the wires *V* to a voltmeter so as to

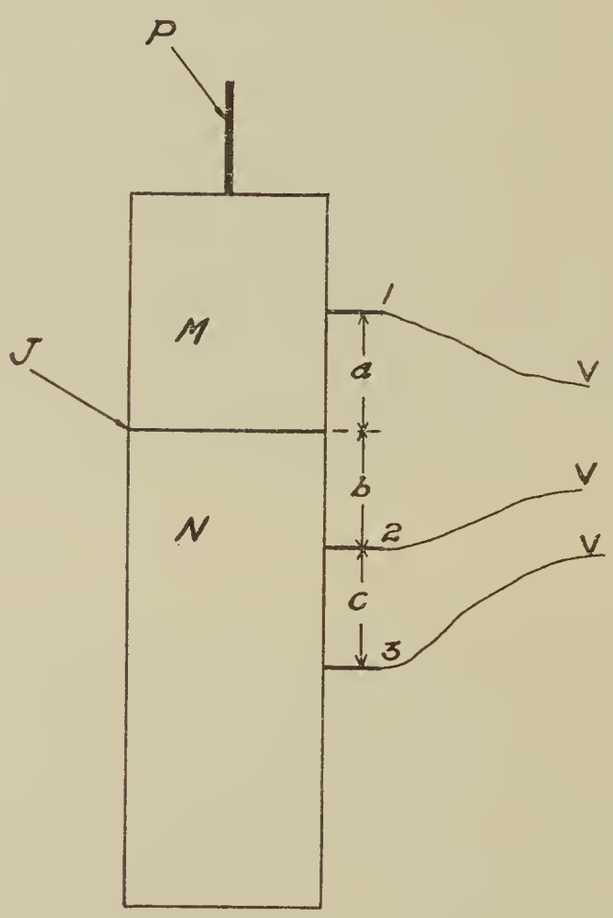


FIG 4.

measure the potential drop along the carbon. The jointed electrode is then used in the furnace in the usual manner, *P* representing the cable carrying the current to the section *M*, while section *N* is in the crucible. While some tests were made with the furnace containing the usual charge of the metal, they were not the most satisfactory, owing to the difficulty of keeping the current steady while determining the voltage drop. Accordingly the most satisfactory experiments were made by filling the crucible with granular carbon, into which the section *N* was plunged to

various depths so as to get determinations of voltage drop with different current densities.

In determining the potential drop, readings of the voltage were taken between *1* and *2*, and *1* and *3*, that between *2* and *3* being determined by difference, for on account of the logarithmic scale of the alternating current voltmeter the potential drop between *2* and *3* could not be read with sufficient accuracy. As the instruments used in the experiments were not calibrated the best method of determining the effect of the joint was to express the joint resistance in equivalent length of electrode. Thus, instead of calculating the ohmic resistance of the joint the resistance is expressed as so many inches or centimeters length of electrode. The calculation is as follows:

Volts between *1* and *2* = E′
Volts between *2* and *3* = E″
Volts drop in joint = E
Distance from *1* to joint = *a* in. or cm.
Distance from *2* to joint = *b* " " "
Distance from *2* to *3* = *c* " " "
Equivalent length of joint = *x* " " "

Then

$$E = E' - \frac{(a + b)\,E''}{c}$$

$$x = \frac{c\,E}{E''}$$

$$= \frac{c\,E'}{E''} - (a + b)$$

RESULTS.

A large number of electrodes which had gone through different manufacturing processes were tested in the furnace simply for the purpose of determining whether or not they would break in use when subjected to the severest conditions, such as overloading, sudden changes of temperature, etc., and as a result much knowledge has been gained as to the causes of electrode breakage.

In order to study the influence of different manufacturing processes on the consumption of carbon under definite conditions

of use a large number of electrodes were manufactured, these being divided into several series. Only one of the numerous factors entering into the manufacturing process was varied in any series, every other condition being kept the same. When the electrodes were made they were tested by the regular laboratory method, and then submitted to the service tests described above. In this particular investigation there has been, so far as the tests have gone, 6 series of carbons tested.

As regards the real density no variations have been found, all electrodes giving the same results. As the attempt was made so to adjust conditions of manufacture that there should be no variation in this physical characteristic the results may be considered as highly satisfactory, and give reasons for believing

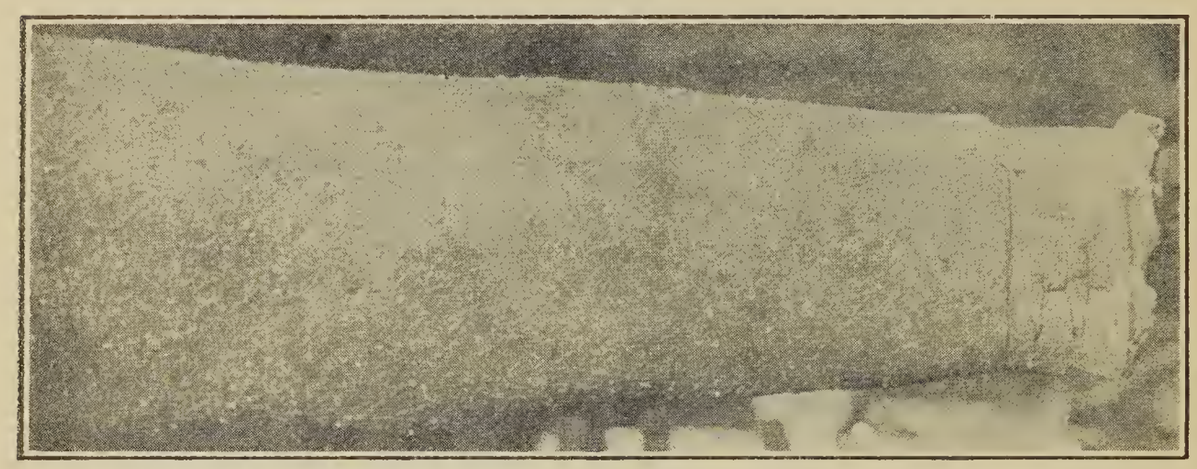


FIG. 5.
Showing consumption of a Vertical Electrode; top at left, botton at right.

that the great variations found in other characteristics were due simply to the deliberate differences in manufacturing process and not to some unknown causes.

Considerable differences were found in the apparent densities of the electrodes tested, these varying from 1.40 to 1.50. The most interesting results, however, were those obtained in determining the kilowatt hours used per unit weight of carbon, for it was found that the extreme variations were as much as 100 percent. The importance of this discovery can scarcely be overestimated as showing the great influence manufacturing conditions may have on electrode economy. Such astonishingly large variations were at first viewed with suspicion, for it was feared that they were really due to the way in which the electrodes were

used in the furnace and not to inherent peculiarities of the carbon. Experiment showed, however, that when tests were repeated the results checked in a satisfactory way.

In testing the jointed electrodes a great number of heats were made so that the behavior of the joint itself when in the furnace could be noted. Fig. 5 is from a photograph showing a partially consumed joint. In one set of tests an electrode was made by joining four 15-inch (380 mm.) sections together, thus making an electrode 60 inches (1,520 mm.) long and 10 inches (254 mm.) in diameter. The electrical connection for the cables was made at the top section, and new sections added to the electrode as it wore away. With this electrode 60 heats were made, the behavior of the electrode throughout being excellent.

Below is given the results of a series of tests made with a 10-inch (254 mm.) round electrode made in two sections, the object being to determine the resistance of the joint expressed as equivalent electrode length. In the tables the first column gives the time at which the measurements were made, in the second column the amperes carried by the carbon, in the third column the equivalent length (x) of the joint in inches, and in the fourth column the same quantity expressed in millimeters.

Test 1:

The end of the electrode was plunged in granular carbon. The test was finally stopped because the roof of the furnace became dangerously hot from the heat radiated from the granular carbon.

TABLE I.

Time	Amperes	x (inches)	x (mm.)
10.03 A. M.	3420	3.4	87
	3560	2.9	74
	3000	2.8	71
	3240	2.8	71
	3480	2.8	71
	3560	2.8	71
	3720	2.7	69
	3900	2.4	61
	2940	2.4	61
1.00 P. M.	2740	2.5	64

It will be observed that the resistance of the joint decreases as the electrode becomes hotter.

Test 2:

The furnace was allowed to cool for 1 hour and 50 minutes after stopping Test 1, and then started again.

TABLE II.

Time	Amperes	x (inches)	x (mm.)
2.50 P. M.	3320	3.9	99
	4200	2.9	74
3.27 "	4260	3.1	79
3.50 "	3300	0.7	18

As a result of cooling the electrode the resistance of the joint was increased, compared with what it had been at the end of Test 1, but after heating for an hour with a very heavy current its conductivity was greatly improved.

Test 3:

This test was made the day after Tests 1 and 2, so that the electrode was allowed to cool down completely. The conditions of the test remained the same as before.

TABLE III.

Time	Amperes	x (inches)	x (mm.)
9.15 A. M.	3300	4.5	114
9.50 "	3400	2.8	71

This again shows the increased resistance of the joint when cold and a great improvement even after a short period of heating.

Test 4:

Heretofore the tests were made with granular carbon in the furnace so that the electrode was not much disturbed. It was now decided to make tests melting small charges of pig iron so that the electrode would be put to the severest possible use, both electrically and mechanically.

TABLE IV.

Time	Amperes	x (inches)	x (mm.)
2.16 P. M.	....	...	..
2.50 "	3900	1.5	38
	4260	1.8	46
3.00 "	3580	1.0	25
3.10 "	4000	1.0	25

Unfortunately it was not possible to get satisfactory readings at the first part of the heat owing to the rapid variations in current, but it will be observed that when the readings could be taken the resistance of the joint was less than at any time since the end of Test 2.

Test 5:

A second heat was started about 18 minutes after the conclusion of Test 4.

TABLE V.

Time	Amperes	x (inches)	x (mm.)
3.28 P. M.	....	...	..
3.52 "	3900	1.8	46
	4020	1.4	36
4.00 "	3900	0.8	20

The highest resistance found in the joint was at the beginning of Test 3, when the equivalent electrode length was 4.5 inches (114 mm.), and this is negligible. The resistance in every case diminished after the electrode had been in use for some time and had, therefore, became heated. On account of the negative temperature coefficient of the electrical resistivity of carbon the electrode itself has a lower resistivity after being in use for some time and therefore having a higher temperature. This effect, however, is eliminated in the case of the joint, because the equivalent length of electrode is always in reference to the electrode itself at the time of making the measurement. The explanation of the phenomenon, therefore, is that the heating of the joint

improves the contact between the sections and the connecting plug. The results given above have been amply confirmed by other experiments.

We must finally acknowledge our great indebtedness to the National Carbon Company, which has borne all the expense of this investigation and has co-operated with us in every way possible in making the experiments.

FitzGerald & Bennie Laboratories,
Niagara Falls, N. Y.

DISCUSSION.

Mr. N. Petinot: The method of joining electrodes mentioned by Mr. FitzGerald is not absolutely new, since for some three or four years the German electrode manufacturers have been exporting such joined electrodes. I had the opportunity to experiment with such joined electrodes, and I found that the joints made in a laboratory are usually good, but in general practice it is quite different; very often the joints get red hot, and for the following reasons: We admit in general practice a current density of 40 amperes per square inch, and the electrode must be able to support an overload of at least 25 percent, by which I mean, must be able to carry 50 amperes per square inch. If we consider two electrodes A and B joined by the nipple C, and that A and B have a section x, and C $x/2$, if the joint between them is not very good, if x carries 40 amperes per square inch, we see immediately that the nipple of the other half of the section will carry 80 amperes, and as the material composing the nipple is not a sufficient conductor to carry off the heat, the nipple and joint will get red hot. I would suggest that the nipple be made of graphite, which can carry 150 amperes per square inch without any trouble.

Another difficulty is to screw a new electrode on a furnace in operation, just stopped for this purpose. I will take the easiest furnace, a steel furnace with an arch cover. Anyone who has had experience with such furnaces knows how hard it is to

send somebody on to the hot roof to perform this operation, and, if we admit that process is difficult, what shall we say when the top is open, as in the case of a 10,000 kw. ferro-silicon or carbide furnace, when it is a hard proposition to stand even ten feet from the furnace.

I think our carbon manufacturers will help very much the development of the electric furnaces which use electrodes if, instead of giving us joined electrodes, they put their efforts to give us some good electrodes fifteen to twenty feet long, such electrodes being clamped by a holder two feet from the working end so that they can be slid in when it is necessary.

Dr. Carl Hering: Mr. FitzGerald states that a better figure than lb. per ton is lb. per kw. hr. It seems to me, also, that that is a better figure than the other, but is that a rational figure? Supposing you lengthen your arc, you will have the same current, you will have greater kw. in the furnace, but would the electrode be strained any more than with the short arc? It seems to me that the figure is a better one than the one usually given of lb. per ton, although the latter figure is really what interests the steel makers.

On page 342 of the paper Mr. FitzGerald states that the variations are as much as 100 percent, but I have not been able to find out from the paper where the losses are.

Mr. C. A. Hansen: Mr. FitzGerald's figure of kw. hrs. per lb. of electrodes consumed is a good one to use for practical reasons.

For instance: With a 2-ton steel furnace melting scrap and making casting steel, the power consumption may vary from 500 kw. hrs. per ton melted to 1,400 kw. hrs. per ton melted, depending upon whether the furnace is melting a full charge or not and whether the furnace is operating continuously or discontinuously. The electrode consumption has, however, been found to be 1 lb. per 25 kw. hours, whether 500 kw. hours per ton or 1,400 kw. hours per ton are consumed in the melting.

The electrode consumption per unit of power is, however, markedly influenced by current density; by voltage in steel furnaces, inasmuch as too low a voltage leads to electrodes dipping in slag and consequent reduction of slag at the expense of electrode carbon; by the nature of the charge; etc.

For instance, in the Week's zinc furnace, where the electrodes arced to each other, the electrode consumption was not over 1 lb. per 500 kw. hours; in the steel furnace previously mentioned, using the same electrodes, currents, etc., but melting iron borings under a deoxidized slag, the electrode consumption did not exceed 1 lb. per 50 kw. hrs.

Dr. W. R. Whitney: Can Mr. FitzGerald tell us whether there is an effect on the life of the electrode, other things being equal, due to the ash or mineral content of the electrode, and whether work is being done in this country or elsewhere to secure electrodes to which have been intentionally added certain mineral substances, and whether experiments have been carried out to see whether carbon electrodes will last longer when something like boric oxide has been added to them.

Mr. A. T. Hinckley: I think work has been done along that line, showing that the various mineral impurities do increase the life of the carbon.

Mr. C. A. Hansen: There seems to be no difficulty in getting high ash content electrodes. I have seen them up to 13 percent ash, and the high ash content makes for very high electrode resistivity—probably because it is associated with the use of coal, and coal in itself gives a high resistance form of carbon when fired at the temperature common to electrode manufacture.

Very long electrodes are perhaps all right for stationary furnaces, but when a tilting steel furnace is used, and the electrodes tilt over with the furnace, long electrodes might often interfere with the crane chains supporting the ladle.

Dr. Carl Hering: There is a point I might call attention to in conjunction with the joined electrodes, which I saw in Chicago, and that was that there happened to be a joint, when we saw the furnace in operation, just outside the top of the furnace, and below the joint the electrode was red hot, while above it was black, which indicates an enormous heat resistance through the joint, which is of some importance in the electrode losses, as the heat loss would be perceptibly diminished by these joints.

Dr. W. R. Whitney: It has seemed to me always, and still seems, as though the carbon electrode was a mighty poor con-

trivance for bringing heat into a furnace. There are probably many ways of improving that condition and making electrodes which will do the same work and not be consumed, or which will be consumed at a slower rate. I think experiments should be made, adding salts such as borates, etc., to the carbon. Boric oxide up to certain temperatures might protect the carbon at red heat.

Mr. F. A. Lidbury: After all, the most important point in connection with the electrode is that it should not break when subjected to reasonable treatment.

Mr. Acheson Smith: Mr. FitzGerald speaks of the apparent density having a marked influence on the life of the electrode, and mentions tests which showed the different electrodes varied from 1.40 to 1.50. I would like to know to what degree the life of the electrode is affected by a given difference in apparent density. That is, how would the life of an electrode having an apparent density of 1.40 compare with the life of an electrode having an apparent density of 1.50?

Mr. F. A. J. FitzGerald: It should be noted that the jointed electrodes referred to by Mr. Petinot were of German manufacture, and that the specially prepared graphite paste used by us was certainly not the same as he used. We have made up electrodes of sections like these, five or six joined together, and in no case was there any heating at the joints.

Mr. Petinot's criticism about the difficulty of joining sections on the top of a hot furnace is correct; it is most disagreeable work. Nevertheless, it can be done, and is cheaper than throwing away half an electrode.

As to making long electrodes, work is being done on that, though I do not know what is the greatest length made by the National Carbon Company—I think something like 100 or 120 inches (2,540 or 3,050 mm.).

In regard to what Dr. Hering said about a long arc causing a great strain on the electrode, that agrees with my experience. In all our tests we used the same E. M. F., fifty volts, except in some special experiments where we were trying to break the electrode by very severe strains. The most annoying thing that can happen in a furnace is the breaking of pieces off the electrode,

and we believe that these experiments have revealed the cause of that breakage. In working on that point we have used arcs of 75 or even 90 volts, giving the electrodes the hardest tests possible; but for the regular service tests we always used 50 volts.

Perhaps we should not have mentioned in the paper anything about the 100 percent variation in life, as we are not prepared to go fully into that matter. The experimental work is still under way, and until it is completed we do not want to publish anything more definite on the subject.

The greatest difficulty in carrying out the suggestion of Mr. Lidbury is to get the manufacturers and users of electrodes to agree on a definition of the word "reasonable."

We cannot reply to Mr. Acheson Smith's question because we have not yet worked out the co-relation between apparent density and life of the electrodes in these series of experiments.

I do not think that the joints Dr. Hering saw in the United States Steel Corporation's work were made with an amorphous carbon electrode.

Dr. Carl Hering: Those referred to were graphite, not carbon.

A paper read before the New York Section of the American Electrochemical Society, February 7, 1913, and called up for discussion at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 3, 1913, President W. Lash Miller in the Chair.

ALUMINIUM NITRIDE

By J. W. Richards.

Introduction.

The production of aluminium nitride (AlN) on a large scale is proposed in the electric furnace process of Ottokar Serpek, followed by the decomposition of the same by water or caustic soda solution, thereby liberating the nitrogen as ammonia and producing alkaline aluminate solution from which pure alumina can be obtained. This rather daring chemical proposition has directed attention to aluminium nitride, the conditions of its formation and its properties.

The existence of aluminium nitride was suspected for some time before it was isolated. A rather indefinite number of years ago, probably about 1890, the attention of the writer was directed by his father to the fact that when metallic aluminium in a melted condition was skimmed, and the skimmings or dross laid to one side, that on pouring water upon them, while still warm, these skimmings gave off an odor of ammonia. The explanation which was then figured out for this phenomenon was that the hot aluminium in the skimmings oxidized to alumina, and that the rather high temperature thus produced locally caused the aluminium to unite also with the nitrogen of the air and form nitride. In other words, that some of the aluminium united first with the oxygen and immediately thereafter some also with the nitrogen of the air. On sprinkling with water the nitride would react according to the following equation:

$$2AlN + 3H_2O = Al_2O_3 + 2NH_3$$

In the light of subsequent investigation and the formation of aluminium nitride in other ways, it appears that the explanation given in these early days was correct and that aluminium nitride

is formed directly under such conditions from metallic aluminium and the nitrogen of the air.

Le Verrier, later, proved the presence of traces of nitrogen in commercial aluminium by dissolving it in caustic potash and passing the nitrogen evolved into Nessler solution, obtaining from it the ammonia reaction. He thus proved the presence of nitrogen in the metal and suspected it to occur as aluminium nitride dissolved in the excess of metal. In further experiments he treated aluminium with a current of nitrogen gas until it was saturated, and noted that this produced considerable diminution in the tensile strength, elastic limit and elongation of the metal.

Prof. Mallet later obtained aluminium nitride corresponding closely to the formula AlN by heating metallic aluminium in a carbon crucible to a moderate temperature for several hours, in contact with dry sodium carbonate. Some alumina is formed, some sodium vaporizes and some carbon is deposited; the reaction is probably as follows:

$$3Al + Na_2CO_3 + N = AlN + Al_2O_3 + C + 2Na$$

Aluminium nitride containing 34 percent of nitrogen and 66 percent of aluminium was obtained as little yellow crystals and amorphous drops. When calcined in the air it was found to lose nitrogen and form alumina; it was decomposed in moist air, losing its transparency, becoming lighter yellow, evolving ammonia gas, and finally leaving the alumina residue. Caustic potash solution and melted caustic potash both attacked it actively, disengaging ammonia and forming potassium aluminate.

A later experimenter described the compound as a gray amorphous powder, but with properties otherwise similar to those described.

The Serpek Methods.

Coming now to the work of Serpek we find his first proposition to be the production of aluminium nitride from aluminium carbide, which is indeed a possible reaction. In his U. S. patent 867,615 (filed June 19, 1906, issued October 8, 1907) he describes the passing of nitrogen or a gas containing nitrogen over aluminium carbide as an initial material heated to red heat. He describes the volume of the carbide increasing as it is converted into nitride,

and that the absorption of nitrogen was increased by diluting the carbide with such materials as carbon or aluminium chloride; also that traces of hydrochloric acid or sulphur dioxide in the gas currents facilitated the conversion. The claims of this patent are essentially for the method of producing aluminium nitrides by heating aluminium carbide in an atmosphere containing nitrogen to a red heat with or without the diluting substances admixed and with or without traces of acid gas in the nitrogen used.

Attention may be called to the term "aluminium nitrides" in this patent, corresponding to the fact that in the product thus obtained by Serpek he found that part of the nitrogen in the product was driven off by contact with air, and a further part by boiling with water, and a still further part by treatment with caustic alkali solutions. These facts pointed to the non-homogeneity of the product, which thus appeared to consist of a mixture of different nitrides instead of one distinctive chemical compound.

Continuing his work, we find that Serpek later concluded that it might be possible to obtain the nitride directly from mixtures of alumina and carbon, which it will be recalled he used as diluent substances in the conversion of the carbide. He was apparently not able at that time to produce nitride directly from these two substances, but found that in the presence of a small amount of a metal, such as copper or iron which is capable of forming an alloy with aluminium the formation of nitride from the mixture took place. In his U. S. patent 888,044 (filed May 24, 1907, issued May 19, 1908) he describes mixing alumina with carbon in the proportions necessary for formation of CO gas ($Al_2O_3 + 3C$), adding about 5 percent of either copper or iron or a mixture of the two, and heating the mixture to a red heat in a current of nitrogen gas, at which temperature the partial formation of an alloy of aluminium, produced by reduction, with the copper or iron would be initiated. The idea seems to have been to produce a mixture on the point of reaction from its constituents and then to super-add the influence of the current of nitrogen gas. Traces of HCl or SO_2 gases are said to facilitate this reaction also, and the product is described as almost pure aluminium nitride. The reaction is described as developing a high temperature as soon as it is initiated. The claims are for producing aluminium nitrides

by heating the mixture of alumina with carbon and a metal capable of forming an alloy with aluminium, to red heat in an atmosphere containing nitrogen, with or without the presence of small amounts of acid gases.

It is evident that in this method the conversion of alumina into aluminium nitride was aimed at, with the assistance of small amounts of metals as catalytic or assisting agents. Whatever may have been the results of this process, it led the investigator in the end to the method described in Serpek U. S. patent 987,408 (filed December 15, 1909, issued March 21, 1911) in which aluminium nitride is produced directly from Al_2O_3 and carbon in the presence of nitrogen, at a much higher temperature than previously recommended. This patent appears to be the result of considerable investigation on the conditions of this direct production, and specifies very exactly the temperatures at which the direct conversion takes place. The patentee speaks of the general supposition that extremely high temperatures would be required for such direct conversion, such as the highest temperatures of the electric furnace, but explains that by careful investigation he had found that if the temperature is closely watched some combination of nitrogen with aluminium can be observed even at 1,100° C.; that at 1,500° nitrogen is absorbed fairly rapidly, at 1,700° energetically, and that at 1,800 to 1,850° the reaction may be almost designated as violent, producing almost chemically pure nitride. Further, Serpek found that temperatures higher than this gave a smaller yield, and that somewhere above 2,000° the production practically ceased, the decomposition temperature of the nitride appearing to be about 2,120° C. This brilliant piece of experimental work really laid the foundation for the Serpek process as it now exists. The inventor further discovered that impure alumina, such as bauxite ore, was converted at somewhat lower temperatures than the pure material, evidently owing to the catalytic effect of the impurities present.

The claims of this patent are for producing aluminium nitride by heating aluminous compounds and carbon, or more specifically alumina and carbon, in an atmosphere containing nitrogen to temperatures not exceeding 2,000° C., and preferably about 1,800°.

Reference may very properly be made at this point to the

experimental investigations and confirmations of these results by Prof. S. A. Tucker and Henry L. Read, given before the Eighth International Congress of Applied Chemistry, published in its Transactions, and in volume XXII of the Transactions of the American Electrochemical Society. This investigation, carried on in the electrochemical laboratory of Columbia University under carefully regulated conditions, showed traces of nitrogen absorbed at temperatures of 1,000 to 1,100° and as much as 30 percent of nitrogen in selected portions of the product made between 1,800 and 1,900°. The product made at higher temperatures contained less nitrogen and was either sintered or fused. Impure alumina, such as bauxite, was found to be converted more easily than pure alumina, and the definite statements of the last Serpek patent were confirmed and verified.

The Serpek Reaction.

The decomposition of alumina by carbon in presence of nitrogen to form aluminium nitride is a reaction which is interesting to study and compare with analogous reactions.

Professor Baron, in 1760, tried to reduce alumina by carbon, but was unable to obtain the temperature required.

Oerstedt, in 1817, devised a way to decompose alumina by carbon, finding that this took place in a stream of chlorine gas, at a low temperature, the products being aluminium chloride and carbon monoxide gas.

$$Al_2O_3 + 3C + 3Cl_2 = 2AlCl_3 + 3CO.$$

This reaction is practically the exact analogue of the Serpek reaction, using chlorine instead of nitrogen. Deville, for instance, who ran this operation on a large scale, remarks that the retort is heated to a uniform dark-red heat (which would be about 600° C.) and that "however fast the chlorine may pass into the retort, it is so well absorbed during three-fourths of the operation that not a trace is mixed with the carbon monoxide escaping." If the query be made as to why the reaction is so easy, thermochemistry gives us the answer: the reaction is exothermic 17,880 calories.

$$\begin{array}{lll} Al_2O_3 + 3C + 3Cl_2 & = 2AlCl_3 + 3CO. & \\ -391{,}600 & + 322{,}000 + 87{,}480 & = + 17{,}880 \end{array}$$

It is profitable to consider in this connection another analogous reaction.

$$Al_2O_3 + 3C + 3S = Al_2S_3 + 3CO.$$

This reaction does not take place at 1,200° C., and we find it would be endothermic (heat absorbing) 180,200 calories. However, the reaction with carbon and sulphur already combined as CS_2 does take place, readily, at 1,000° C., and this reaction is much less endothermic than with C and S separately:

$$Al_2O_3 + 3CS_2 = Al_2S_3 + 3COS$$
$$-391{,}600 + 87{,}000 + 124{,}400 + 111{,}090 = -69{,}110$$

Coming now to the nitrogen reaction, we have:

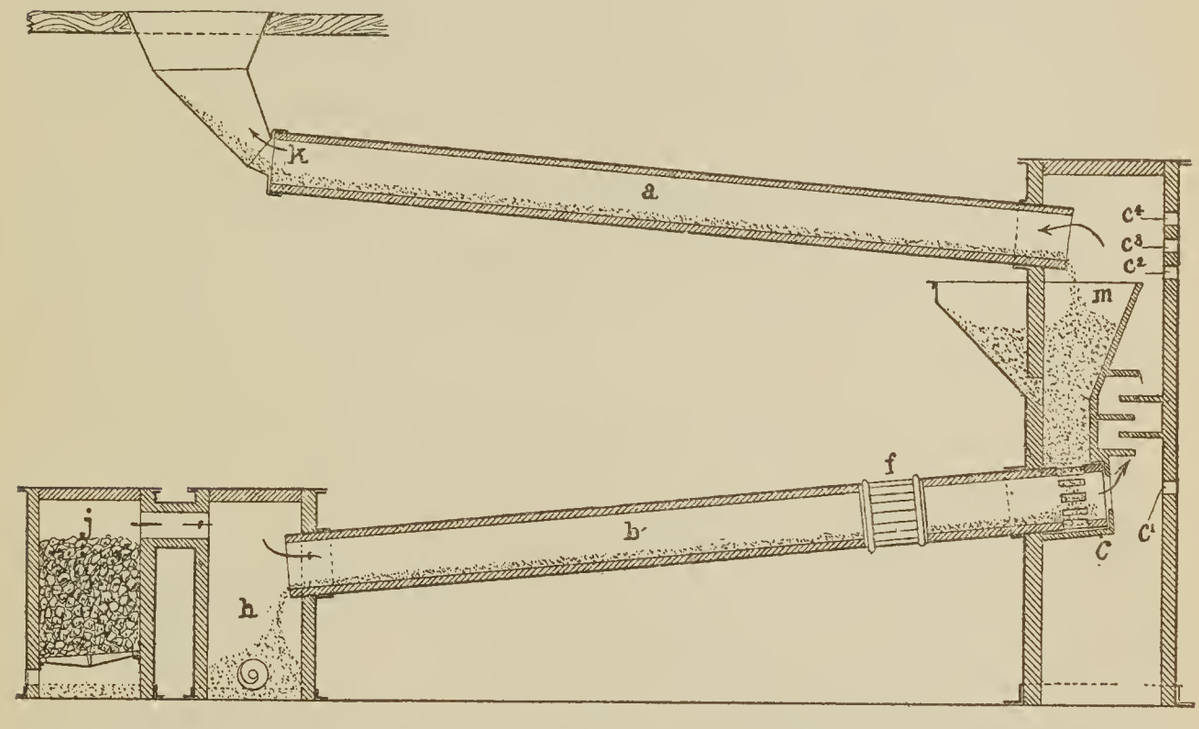
$$Al_2O_3 + 3C + N_2 = 2AlN + 3\ CO$$
$$-391{,}600 \qquad\qquad + 90{,}900 + 87{,}480 = -213{,}220$$

This is therefore a highly endothermic reaction, and corresponding with that we have the fact that it does not take place to an appreciable extent below 1,500° C. Aside from all thermal losses, we can say, therefore, that the reaction itself absorbs 213,220 calories = 248 kw. hours for 82 kg. of aluminium nitride formed; which equals 3,000 kw. hours = about ⅓ kw. year per ton of nitride. At least double this amount would be required in practice.

The Serpek Apparatus.

Serpek's U. S. patent 996,032 (filed June 21, 1910, issued June 20, 1911) contains a detailed description of apparatus intended for the commercial manufacture of the nitride from bauxite or other aluminium ores. The plant consists of two superposed rotating cylindrical kilns, similar in construction to a cement clinkering kiln. These kilns are inclined in opposite directions, so that the material being preheated in the upper kiln and passing from right to left, for instance, falls into the opening of the lower kiln for treatment at higher temperature where it passes from left to right. Bauxite alone is passed through the upper kiln, and there calcined; then mixed with the necessary carbon in its passage from the upper to the lower kiln, and the mixture treated by nitrogen at a high temperature in the lower kiln, which is provided with a detachable electric resistance furnace about midway of this length and which is intended to

subject the charge therein to the reacting temperature, about 1,800 to 1,900° C. The material is discharged from the lower end of this kiln into an air-tight receiver. A large gas producer of the ordinary type furnishes producer gas (approximately ⅓ CO, ⅔ nitrogen) to the lower end of the lower kiln. This gas entering at a temperature of about 400° becomes highly heated as it passes through the kiln in a direction contrary to the descending charge, and at the electrically heated zone at a temperature of 1,800° to 1,900° reacts upon the mixture, forming



Serpek Apparatus: *k*, supply of ground bauxite and gas exit to chimney; *a*, calcining kiln; *m*, hopper in which calcined bauxite mixes with carbon; *b*, kiln for nitride reaction; *f*, electric resistance furnace; *h*, storage chamber for hot nitride; *j*, gas producer; *c*, chamber for deposition of fumes and dust; c^1 c^2 c^3 c^4, air inlet for combustion of gases from lower kiln. From Serpek U. S. Patent 996,032.

nitride. After leaving the high temperature zone the gas enriched in CO coming from the reaction preheats the descending charge, issues from the upper end of the kiln into a vertical closed chamber and passes through it to the opening of the upper kiln, where it meets a blast of air which burns it for the purpose of heating the contents of the upper or calcining kiln.

The apparatus as thus described achieves a methodical heating of the reacting mixture, utilizes the CO gas made in the producer and also that evolved by the reaction in the furnace; aims at an intimate mixture of the charge by the rotation of the cylinders and intimate contact of the nitrogen with the charge. The in-

ventor states that the silica impurity of the charge is mostly volatilized (probably as reduced silicon) from the charge at the reacting temperature and is thus carried out in the gases; and that the apparatus may be used for producing other nitrides made by analogous reactions.

The claims cover an apparatus comprising the features of a revolving inclined upper cylinder discharging into an inclined lower cylinder revolving in the opposite direction, through a vertical chamber in which the gas from the lower cylinder may be burned, combined with a detachable electric resistance heating furnace within the lower cylinder. One claim is for the single feature of a rotary calcining cylinder carrying a detachable electric resistance furnace.

Undoubtedly a large amount of excellent investigation has been put upon this process, and it certainly deserves commercial success. The method is being tested in France upon a large experimental scale.

DISCUSSION.

Mr. C. W. Bennett: What is the effect of moisture on this reaction? Has it the effect of raising the temperature of the reaction, or of causing decomposition?

Prof. Jos. W. Richards: With the apparatus shown, it will be impossible for any water to come in contact with the material during the reaction, because the material is calcined in the upper kiln, and the water driven out of it before it goes into the reaction chamber; the gases used pass through the gas producer, so that there will practically be no water vapor in the gas. If there were water vapor passing through, I do not think it would react on the nitride at these temperatures, for it is found that hydrogen in the gas lowers the temperature at which the reaction takes place, and, so far as that is an indication, it would show that the reaction worked the other way, and so water vapor can have no effect in hindering the reaction. Serpek speaks distinctly of small amounts of other gases having a facilitating effect upon the reaction, and particularly that a small amount of hydrogen makes the reaction proceed at a lower temperature.

A paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 3, 1913, President W. Lash Miller in the Chair.

SOME TESTS OF THE EDISON STORAGE BATTERY

By C. W. Bennett and H. N. Gilbert.

The Edison battery, as developed by the Edison Storage Battery Company, is an extremely important addition to electrochemical apparatus. This is realized when it is remembered that the equivalent of about 300,000 150-ampere-hour cells are being used today. The performance and properties of this battery have been studied exhaustively by the Edison Company only. A few of the papers[1] which have appeared in the literature on this subject may be referred to. These have dealt with the manufacture, details of construction, and performance of cells operating at normal rates. In view of the fact that this information is meagre, it was thought that measurements from a different standpoint, made by different workers, would be of value.

For these measurements a battery of four cells was loaned the Department of Physical Chemistry by Dr. E. W. Brown, P. A. Surgeon, U. S. N. The battery being available only for a short time, it was decided to run a few efficiency tests at different rates of discharge, study the effects of charging at different rates, check the measurements of capacity, and study the cell operating at a low temperature.

[1] Kennelly: Trans. Am. Inst. El. Eng., **18**, 219 (1901).
Roeber: El. World and Eng., **37**, 367 (1900); **38**, 931 (1901).
Marsh: El. World, **39**, 996 (1902).
Hospitalier: L'Industrie Electrique, **12**, 493 (1903).
Jungner: Electrochem. Ind., **1**, 258, 465, 508 (1903).
Schoop: *Ibid.*, **2**, 272, 310 (1904).
Silg: *Ibid.*, **3**, 237 (1903).
Jououst: L'Eclairage Electrique, **38**, 201 (1904).
Hibbert: Jour. Inst. Elect. Eng., **33**, 203 (1904).
Joly: *Ibid.*, **33**, 226 (1904).
Kennelly and Whiting: Trans. Am. Electrochem. Soc., **6**, 135 (1904).
Thompson and Richardson: *Ibid*, **7**, 95 (1905).
Elbs: Zeit. Elektrochemie, **11**, 734 (1905).
Zedner: *Ibid.*, **11**, 809 (1905); **12**, 463 (1906).
Faust: *Ibid.*, **13**, 161 (1907).
Foerster: *Ibid.*, **13**, 414 (1907).
Holland: Electrician, **68**, 165 (1911).
Montpellier: Lumière élec., **16**, 244 (1911).
Lyon: Jour. Ind. and Eng. Chem., **3**, 922 (1911).
Schneckenberg: Electrochem. Zeit., **19**, 1 (1912).

The cells used were the standard type, A 8, 300 ampere-hour cells, normal charging and discharging rates 60 amperes. The cells were connected in series.

In order to obtain these data in the course of the short time which the cells were at our command, it was decided to charge the cells until the voltage had remained practically constant on the highest part of the curve, for one hour. This was therefore called a complete charge, instead of the seven hours run at 60 amperes, as recommended by the Edison Company. The battery was therefore completely charged, and then discharged at the desired rate until the voltage on closed circuit was 0.7 volt per cell. The amount of energy necessary to bring the battery back to the original voltage was taken as the proper input for the calculation of efficiency.

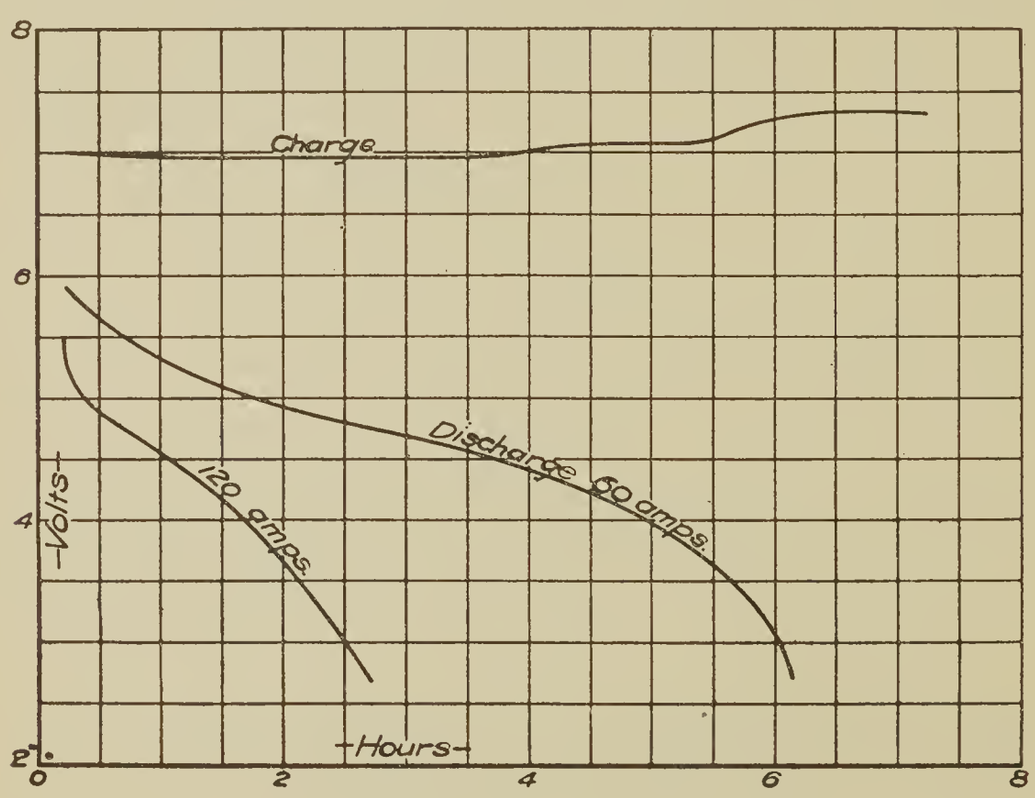


FIG. 1

Recording meters were used and the mean voltage obtained from the equation:

$$I = \sqrt{\frac{2a}{\infty}}$$

where I = mean radius measured on a chart, which of course corresponds to the mean voltage, a = area of the sector bounded

by the voltage-time curve and the radii extended to the center of the chart, and α = the angle in radians which was subtended by the time-voltage curve. The area was obtained by a planimeter, the angle being measured in degrees. The current of course was constant. The meters were carefully calibrated, and the errors introduced minimized as much as possible.

For comparison, Fig. 1 shows curves for charge and discharge at 60 amperes and one discharge at 120 amperes. For the normal charge it is seen that the average voltage is about 7 volts for the battery, the average discharge voltage being 4.5 volts, or 1.12 per cell. It is seen that the voltage continuously decreases upon discharge. The actual figures for curves A and B are as follows:

TABLE I.

Ampere-hours input	410
Ampere-hours output	350
Ampere-hour efficiency	85.4 percent
Watt-hours input	2874
Watt-hours output	1589
Watt-hour efficiency	55.3 percent

It has been stated that the Edison battery is capable of operating at high rates. No actual figures however are available as to what energy efficiencies or capacities are obtained under these conditions. The figures given below are not extremely accurate, for they only represent one measurement each. They do, however, give an idea of what may be expected from these cells. Below are given efficiencies for four rates of discharge, the charge being normal. The output of the four cells is also given.

TABLE II.

Discharge Rate in Amperes	Average Voltage	Watt-hour Efficiency (Percent)	Output	
			Ampere-hours	Watt-hours
60	4.55	55	350	1593
120	4.30	53	260	1118
200	3.80	38	225	855
270	3.50	32	180	630

The decrease in efficiency as well as capacity is seen from curves in Fig. 2. From these figures it may be concluded that

the battery is capable of operating at high rates with a remarkably small decrease in efficiency and capacity. An astonishingly small decrease in the average voltage is also noted at the higher rates of discharge.

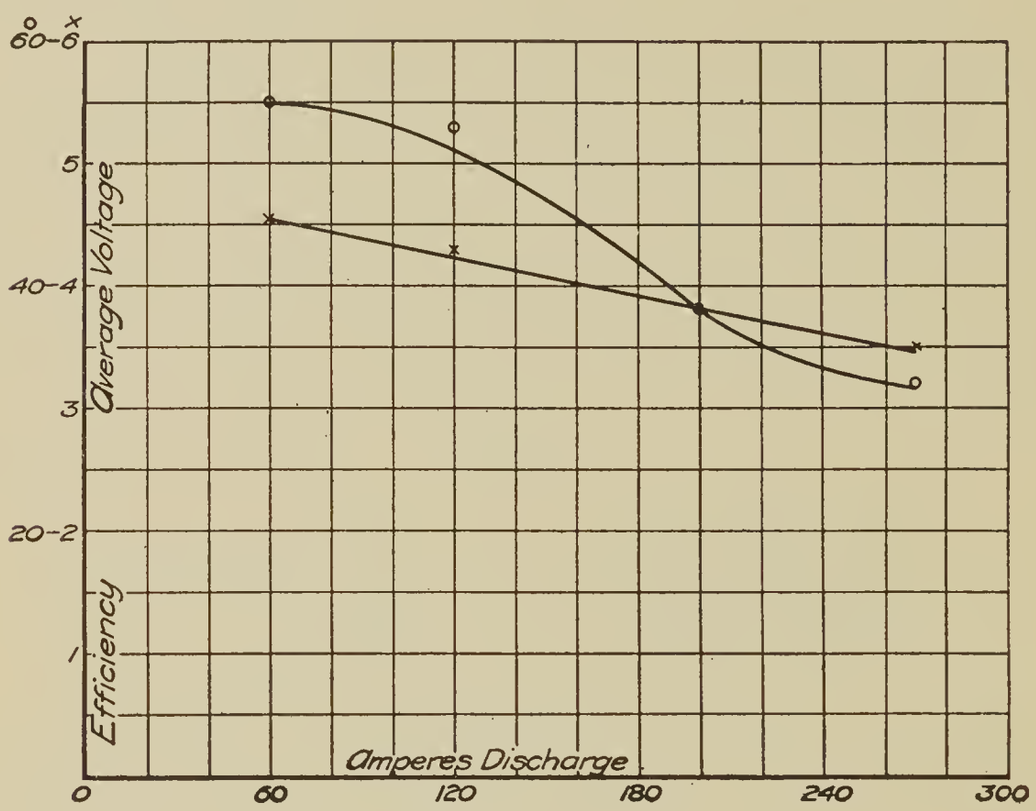


FIG. 2.

It is stated that "booster" charges can be given these cells in practice. It was therefore decided to try some abnormal charging rates, discharging at the normal rate, calculating efficiency.

Below are given some of these tests:

TABLE III.

Charge	Watt-hours		Watt-hour Efficiency (Percent)
	Input	Output	
2 Hours at 120, balance at 60 Amperes	3143	1463	46.5
1 Hour at 200, balance at 60 Amperes	2941	1536	52.2
1 Hour at 300, balance at 60 Amperes	3958	1543	39.0

With the "booster" charge of 200 amperes the charge was complete in about four hours and twenty-five minutes, the battery giving considerably over its rated output on discharge, the efficiency being about the same as for the normal charge.

The Edison cell is said to lose about 10 percent of its charge upon standing 24 hours, after which there is practically no loss. It was therefore decided to allow the charged battery to stand 30 hours and then measure the output upon discharge. It was found that the voltage of the battery had dropped to about 6 volts, and upon discharge the following was obtained:

TABLE IV.

Discharge, after standing 30 hours, at normal rate.

Initial Voltage	Average Voltage	Output	
		Watt-hours	Ampere-hours
5.98	4.54	1384	305

The loss in capacity is about 10 percent of the normal output. In order to see if this loss could not be avoided in cases where a battery is not to be used for some time after charging, it was decided to charge the battery to a definite voltage and discharge from this, taking the output. This arbitrarily selected voltage should be higher than the open-circuit voltage of the battery after standing 30 hours. The drop across the battery on charge upon momentarily closing the circuit was found to be about 16 percent higher than the cell voltage upon open circuit. It was therefore decided to charge the battery until the drop across it was 16 percent higher than the voltage of the battery after standing 30 hours. The charge was therefore maintained until the voltage was 7.1 volts.

The following was obtained:

TABLE V.

Battery charged to 7.1 volts and discharged at normal rate.

Input		Output		Energy Efficiency
Watt-hours	Ampere-hours	Watt-hours	Ampere-hours	
2101	315	1343	290	64

From this it may be seen that the output is practically the same as that for the discharge after standing 30 hours. The efficiency is very good under these conditions, and on the basis of a charge of this nature it seems as if the battery can approach favorable comparison with the lead cell in regard to efficiency. A measurement should have been made by charging up to this voltage, allowing to stand for 30 hours, to show that under these conditions there is practically no loss of the charge. On account of limited time, however, this could not be done.

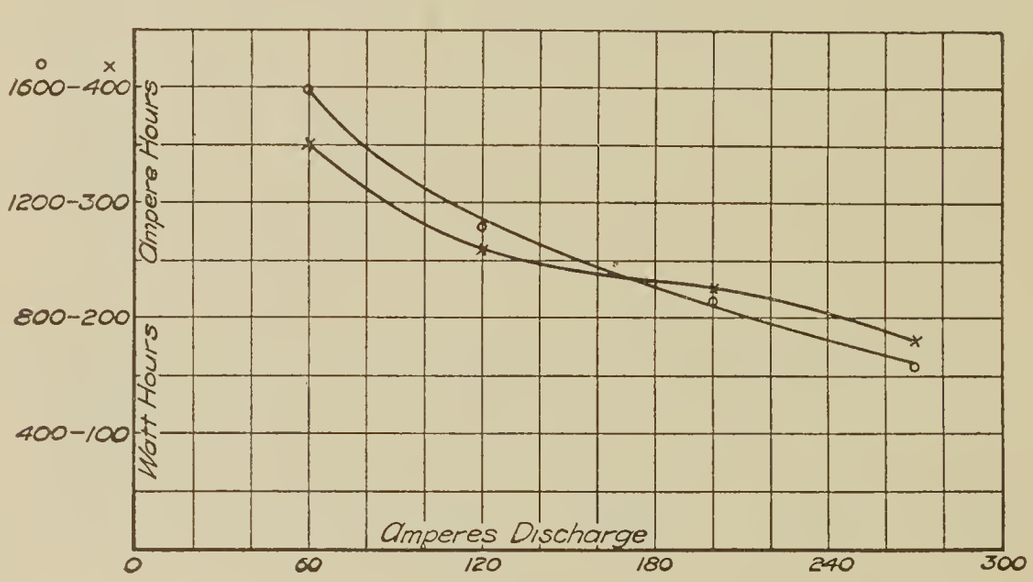


FIG. 3.

In reference to the effect of low temperatures, it may be said that one charge and one discharge was obtained in an ice-water bath, the temperature of the battery being kept at 4° C. The results of a charge at 4° C. of the previously completely discharged battery, at ordinary temperatures, and the corresponding discharge are given. The efficiency cannot properly be calculated from these.

TABLE VI.

Charge and discharge at 4° C. at normal rate.

Average Voltage		Ampere-hours		Watt-hours		Duration, Hours	
Charge	Discharge	Input	Output	Input	Output	Charge	Discharge
7.36	4.46	396	233	2920	1037	$6\frac{2}{5}$	$3\frac{7}{8}$

A very marked effect is obtained here. The voltage difference between charge and discharge is abnormally high.

The battery was later charged at the normal rate under ordinary conditions. This charge gives data for calculating efficiency comparable with that given above. This is the normal use of the cell in cold climates. In cars, of course, the battery would receive discharge at low temperatures on the road, and be charged at room temperature in the garage. The results follow:

TABLE VII.

Charge after discharge at 4° C.

Average Voltage	Input		Efficiency Calculated on Previous Discharge (Percent)
	Ampere-hours	Watt-hours	
6.94	460	3190	33

The fact that more energy was required for this charge than for the previous one probably means that nickel peroxide was not formed at 4° C., probably because the charge was not maintained long enough. If not accurately, the tests show, however, that there is a larger voltage difference between charge and discharge at low temperatures than under normal conditions. The efficiency must, therefore, be lower than normal.

Conclusions.

From what has been said and from experience with the Edison cell it may be concluded, that

1. The energy efficiency, at the normal rate of operation, is about 55 percent, the ampere-hour efficiency being about 85 percent.

2. The cell is capable of operating continuously at high rates.

3. At the 40-minute discharge rate, with charge at the normal rate, the energy efficiency is about 32 percent, the ampere-hour output being about 60 percent of the rated output.

4. The cell can be charged at high rates, the efficiency being about normal when a "booster" charge at 3⅓ times the normal

rate, for one hour, was given the cell. There is no reason why the cell should not be charged at 5 times the normal rate for a few minutes.

5. If the cell is to be charged the day before it is to be used, energy is conserved if the charge is maintained until the voltage reaches about 1¾ volts, instead of carrying it to completion. In other words, no nickel peroxide should be formed on charging, the loss of energy on standing being due, presumably to the spontaneous decomposition of this compound.

6. If the charge is stopped before the higher oxidation products of nickel are formed, the efficiency is higher than normal, being about 64 percent.

7. At 4° C. the battery is capable of delivering more than two-thirds the normal output, when charged at the same temperature. The voltage, of course, is lower than normal, for the internal resistance of the cell is higher at the lower temperatures. The efficiency also is low.

8. The cell may unquestionably be allowed to stand an indefinite length of time without injury.

9. The flexibility is so great that the cell can be used under the most adverse circumstances.

10. The method of charging until the voltage has remained constant for one hour gives satisfactory results, but requires watching or the use of a recording voltmeter.

11. The continuous drop in voltage on discharge (about 10 percent per hour) is a disadvantage against this cell, over the lead cell.

12. When referred to equal amounts of power delivered, the Edison battery weighs about 25 percent less and costs about 25 percent more than the Iron-clad Exide battery.

Electrochemical Laboratory.
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DISCUSSION.

A MEMBER: After the charge is reasonably near completion, does it have the tendency, such as the Exide battery shows, to loosen up the active material? What value has this cell for starting purposes for automobiles, where the discharge rate is exceedingly high? Has it been used for that purpose extensively?

I do not quite understand conclusion 11, where you speak of the ten percent. loss in voltage. Do I understand that the loss is ten percent if the battery stands for twenty-four hours and there is no further loss?

MR. C. W. BENNETT: The active mass of the Edison cell cannot be loosened by excessive charges and discharges. The cell is constructed with the active material placed in perforated nickel-plated steel containers so that the active mass cannot get out, the perforations not being large enough. The cells which have been put on the market have not failed due to faulty construction. The mechanical design of these cells is ideal. The iron oxide is placed in rectangular shaped containers and the nickel oxide in containers in the form of pencils or cylinders of perforated nickel-plated sheet steel, wound spirally to form a cylinder. The nickel oxide is placed in this cylinder and nickeled steel rings placed around the cylinder to prevent bursting. These pencils are then mounted so that the spiral twists of adjacent ones are in opposite directions. Thus unequal strains, occasioned by their tendency to unroll, will not buckle the plates.

In reference to the high discharge rates the cell can be discharged at practically any rate for short intervals of time without any damage whatever. It may be short-circuited numbers of times and goes on performing its work on normal running just as if nothing had happened to it. Presumably, therefore, it can be used for short-circuit or large loads continually. The widest use of the Edison cell, I imagine, is in traction work where, of course, it may be called upon for rapid discharge rates.

In conclusion 11 I refer to the continuous drop in voltage of the cell upon discharge and not to a loss of voltage. The curve for the lead cell, plotting time against voltage, shows a smaller

slope than the analogous curve in the Edison cell. The complete discharge of the lead cell at normal rate is considered to be a discharge to a voltage which represents 10 percent less than the normal average. In the case of the Edison cell the drop in the curve shown in the figure is approximately 10 percent per hour. The drop in the curve shown by the Edison Company is not quite so great, being probably 7 percent per hour. The conclusion nevertheless remains that the continuous drop with discharge is much larger in the Edison than in the lead cell. The curves can be plotted, of course, so that the voltage appears fairly constant by a judicious selection of co-ordinates, the slope of the curve being greater the larger the divisions on the voltage axis. The change of voltage at abnormal rates, however, is markedly in favor of the Edison cell.

Conclusion 11 should not be confused with the statement as to the loss of capacity upon standing twenty-four hours. About 10 percent of the ampere hour capacity of the completely charged cell is lost by standing for approximately thirty hours. After that the loss of voltage is practically zero. This loss is presumably due to the decomposition of the nickel peroxide formed at the end of the charge. After this peroxide is decomposed the normal oxide, Ni_2O_3, is quite stable and there is practically no further loss of capacity.

Dr. Carl Hering: If the discharge is stopped about half way down the curve, and you give the battery a rest and start again, what would the second curve be like? Does it go back to the original voltage?

Mr. C. W. Bennett: The voltage does not go back to the original value because the final value obtained by discharge is the voltage generated by a mixture of the two oxides Ni_2O_3 and NiO, for instance. The discharge forms a larger percentage of NiO and therefore the voltage generated by this mixture will be lower than by a mixture containing less of this oxide. There are also two other factors, namely, diffusion in the electrolyte and temperature. Diffusion would tend to increase the voltage slightly, but upon standing the temperature would drop and therefore when the discharge was started the internal resistance of the cell would be higher. A combination of these three factors

would require that the voltage, after remaining idle, be lower than that at first, so that upon stopping the discharge and starting it up again after waiting, we would obtain a curve consisting of a series of breaks, each portion of the discharge starting at a slightly lower voltage than the preceding one.

Dr. Irving Langmuir: I remember hearing it said that one advantage of the Edison battery was the remarkable constancy of its voltage, since the electrolyte is not used up during the charge of the battery, whereas in a lead cell there is a marked change in the concentration of the sulphuric acid, which in turn causes a change in the electromotive force. I would ask whether it is known what causes the change in voltage of the Edison battery. Is it simply due to internal resistance? If after the battery has been partly discharged the current is shut off and the actual static potential measured, is that found to be practically constant, or does it also decrease as the battery is discharged?

Mr. C. W. Bennett: The factors determining the voltage of this cell are not definitely known. On charge oxygen is taken from the iron plate to the nickel plate. On discharge the reverse operation takes place, so that the cell has been characterized as an oxygen lift cell. The oxygen is obtained from the water forming the electrolyte, the transfer being taken care of, of course, by diffusion, so that there must be some concentration effects when hydrogen and hydroxyl ions are considered. These concentration effects, however, are not of great importance on account of the fact that water is always present in large excess. In the case of the lead cell, of course, sulphuric acid is used up and must be supplied by diffusion, so that, sulphuric acid not being present in large excess, concentration effects are important. On account of the fact that these concentration effects are of minor importance, the Edison cell may be operated at high rates, at rates, in fact, prohibitive in lead cell usage. Another factor determining the voltage is the active material itself. The nickel peroxide forms a single phase with the Ni_2O_3. On account of the gradual decrease in voltage of the cell throughout the charge, it also seems probable that the Ni_2O_3 forms a single phase with the NiO or some intermediate oxide. As the composition of these phases gradually changes, the voltage will also gradually change.

The third factor determining the voltage of the battery is the internal resistance of the cell. The internal resistance decreases with rise of temperature, so that the voltage depends to a marked extent on the temperature, the voltage change with temperature being greater than in the lead cell.

Dr. Carl Hering: Is there any indication in the ordinary discharge of the cell as to how far it is discharged? The lead cell gives some indication of how much charge is left. Is there any indication in this cell?

Mr. C. W. Bennett: This is one of the great disadvantages of the Edison cell. The voltage generated by the cell depends very markedly on the temperature, and after the cell has been running for a definite length of time the temperature is raised and the voltage is of definite value. On standing for a while the voltage will be different, due to the fact that the temperature is different. Dr. Parsons has suggested that, the drop in voltage being more or less continuous and more rapid than in the lead cell, the measurement of the voltage curve could be used for the determination of the state of charge or discharge with greater accuracy than in the case of the lead cell. The difference of potential during the charge of the battery is very nearly constant over a greater part of the charge, so that measurement of the voltage could not be used for determining whether a cell was one-third charged or two-thirds charged. The rise of the voltage at the end could be used just as in the case of the lead cell.

Dr. Carl Hering: How about the gravity in the lead cell?

Mr. C. W. Bennett: You can tell by the gravity.

Dr. Carl Hering: Can you tell by the gravity of the Edison cell?

Mr. C. W. Bennett: I do not think so. The specific gravity of the electrolyte is practically unchanged during the operation of the cell. Water is used up, but it is only a small amount, so that the concentration change is very slight indeed.

Mr. H. H. Smith: I have jotted down a few observations that I have made regarding this subject, having received an advance copy of the paper.

This paper is significant of the growing importance of the storage battery in the electrical and electrochemical industries of this day. It is to be greatly desired that investigations of such apparatus be made by independent workers, for, as is stated in the paper, very little has thus far been published concerning the Edison battery that has not been inspired or actually done by the company manufacturing the battery. Most of the other literature available is referred to at the foot of the first page of the paper, and, being more or less obsolete, it is not accurately applicable to the battery of the present day. Just a word of the history of the battery will make this clear.

The invention of the alkaline battery by Edison was first made known in 1900 or 1901. It was at this time, however, not in commercial form and it was not until 1904 that the battery was placed on the market. Even then its mechanical structure was such as to cause apprehension of its success, and in a very few months it was withdrawn from the market and further experimentation was entered upon. In 1908, the battery was placed before the public in its present form. The structure was radically changed, and this resulted in a change of the electrical characteristics to some extent, and it is for this reason that literature dated prior to 1908 is not to be relied upon in connection with the present type of battery. It will be noted that the dates of the articles referred to are nearly all prior to 1908. Practically the only independent report of any importance that has been presented since that time is the one of the Electrical Testing Laboratories of New York City, presented before the convention of the Association of Edison Illuminating Companies in 1910. This report embraces a very complete investigation made at the instigation of the central station interests in New York, and it checks up the figures published by the battery company in all important details.

It is a matter of disappointment that the paper under discussion was prepared under necessarily hurried conditions, and that conclusions are based upon very incomplete evidence. It is well recognized that physical data based upon isolated experiments cannot be thoroughly reliable; and this is especially true of electrochemical data where local conditions have an important effect upon results. It is stated in the paper that, at least in

part, "the figures given are not extremely accurate, for they only represent one measurement each." It is further stated that recording meters were used, and it has been my experience that these instruments are not satisfactory for storage battery investigations where a small number of cells are used, because of the fact that the values obtained are greatly multiplied under service conditions in which batteries consisting of a large number of cells are employed. My skepticism of the methods and instruments used is based not only upon my own experience, but also upon the fact that a number of inconsistencies are to be found in the results recorded.

Let us consider Fig. 1, on page 360. I have had this curve very carefully replotted, and some of the facts then made apparent may be stated as follows:

The input as indicated by the curve is 435 ampere-hours, whereas in Table I, on page 361, the input is stated as 410 ampere-hours. The output indicated by the curve is 368 ampere-hours, and in Table 1 it is stated as 350 ampere-hours.

On page 361 in the text, just above Table I, the average voltage of discharge is stated as 4.5 volts (1.125 volts per cell); in Table 2, at normal rate, it is stated as 4.55 volts (1.140 volts per cell) and a measurement of the curve in Fig. 1 reveals an average of 4.64 volts (1.16 volts per cell). And further, even this figure is considerably below the established discharge voltage of the Edison battery at normal rate, namely 1.20 volts per cell.

It is needless to go over the paper in detail in this fashion, but I would draw attention to one or two of the statements made in the conclusion on pages 365 and 366. Conclusion No. 5 is here stated as an established fact. It will be noted that in the paper there is absolutely no evidence produced to substantiate this statement, and it is, therefore, merely an assumption. Conclusion No. 11 is hardy accurate. Reference to Fig. 1 shows that the drop in voltage during discharge is, throughout the main portion of the curve, not more than 4 percent per hour, and even this is considerably more than is usually found. Other items might be mentioned, but it hardly seems necessary.

The spirit which inspires such investigations as this one should be highly appreciated by the profession, but it is to be sincerely

hoped that where such widespread and important publicity is to be given the results, as in this case, every precaution will be taken and every effort made to insure the reliability of the data to be published.

DR. W. LASH MILLER: Do these differences you find in the table of losses, and seen all through, vitiate the results of the paper, or are they relatively unimportant?

MR. H. H. SMITH: They are relatively important, as you will see by taking, for example, a battery of 60 cells, the voltage at 1.2 would be considerably more than the voltage at 1.12 per cell, and the difference between the two voltages, would be of very considerable importance in the design of a motor for an electric car, for example, and in a great many other cases. That difference, which is here recorded, is a very great difference in storage battery investigation.

DR. W. LASH MILLER: I think the voltage does make a difference. You spoke of some other matters earlier; the capacity of 368 ampere-hours as against 350 ampere hours?

H. H. SMITH: That makes a difference of something near 5 percent. I quoted such figures to show the curves are not strictly correct..

DR. W. LASH MILLER: The curve has not been accurately drawn?

MR. H. H. SMITH: A circular chart was evidently used in taking these voltage readings, and I think there are probably inaccuracies in plotting, and in fact the shape of the curve is not a characteristic one, due to the inaccuracy, probably, of the recording meter. In my investigations I have not had any great success with recording instruments in getting accurate figures. It seems necessary to use precision indicating meters in this work with readings taken very frequently.

MR. C. W. BENNETT: This is a very inopportune criticism of this paper, because practically every criticism the gentleman has made is stated in the paper. The measurements are published as first approximations, with a view to publishing more complete data later or encouraging the Edison Company to publish the data that they have. There has been absolutely nothing published

as to the energy efficiency of the cell operating under abnormal rates.

Dr. W. Lash Miller: I think that is stated in the paper.

Mr. C. W. Bennett: From a conversation with Mr. Hutchison, it was found that the efficiency of 55 percent, being the average of three runs at the normal rate used, was a little lower than that claimed by the company, which is 60 percent. The average voltage is also a little lower than that claimed by the company.

In reference to the curves in Fig. 1, I am very sorry that limited time prevented my having the curves drawn over, as there was a mistake made by my draftsman in getting up the curves.

Dr. W. Lash Miller: We will give you an opportunity to correct any error of that kind.

Mr. C. W. Bennett: I do not think there are any inaccuracies in the curves. The error in drawing spoken of refers to the fact that these curves do not begin at zero, as may be seen by referring to Fig. 1. When this is taken into consideration the ampere hour output and input of the cell checks up with the data given in Table 1. There can be no discrepancy between the two cases. They were taken from the same data sheet.

In regard to average voltage the same statement is applicable here. These curves have been assumed, I think, to extrapolate to zero, so that the error in the gentleman's added voltage is at the higher value, giving the value higher than the average voltage, as given in the data in Table 2. The gentleman has criticized the curves, and has attempted to explain the idiosyncrasies of these, by the fact that they were taken by recording meters. The curves shown in Fig. 1 and the data given in Table 1 were not taken by recording meters. The normal rate curves represent averages of three determinations taken by an instructor in electrical engineering in Cornell University, and represent actual readings of calibrated Weston meters, readings taken every five minutes at the beginnings and at the ends of the curves, and every 15 minutes over the central part, so that these values are absolutely correct measurements and are put down here as a statement of experiments carried out on the Edison battery.

They are absolutely impartial and should be received as such. The recording meters which were used for the remainder of the measurements were checked upon normal charge and discharge with the actual measurements. In other words, we have calibrated the recording meters under actual running conditions, obtaining calibrations for charge and discharge, keeping a check on the meters at intervals of half an hour by readings on indicating meters kept in the circuit all the time. The amount of current required to run the voltmeter was also taken into account.

In reference to conclusion 5 we have shown, as has been stated in Table 5, that the energy efficiency is 64 percent, if the cell is charged up to about 1.8 volts, instead of carrying the charge to completion. Aside from any consideration of the formation of nickel peroxide, this increased efficiency must show up as a saving of energy.

In regard to conclusion 11, concerning the continuous drop in voltage, the total voltage drop in the normal rate curve is practically 55 percent, or a drop from about 5.85 to 2.75, representing, when distributed over less than six hours, between 9 and 10 percent per hour. From a glance at the curves it may be seen that the drop in voltage is fairly evenly distributed over the curve.

Mr. H. H. Smith: I hope that the spirit in which I offer this criticism will not be misunderstood. You can all appreciate that it is not desirable that there be published such figures as have been named, especially with regard to the voltage, which, as I have tried to show, and which I think you will see, is an important matter.

There were so many inconsistencies, only a few of which I mentioned, found in checking over the paper, that I felt to quote a few of them would justify me in my criticism on the voltage, which is one of the more particular points I wish to bring out.

I will stand corrected with regard to my figures concerning the capacity represented by the curves, because I did not understand when I saw the curves, what that gap meant, and I concluded it meant that readings were not taken between the zero point and the point at which the first reading was plotted, and therefore I figured the ampere-hours from the zero point on the curve.

Mr. C. W. Bennett: On conversing with Mr. Smith, I find that the explanation of the fact that the average voltages of discharge as given in our paper, are lower than those obtained by the Company, is the fact that they discharge to one volt while in our experiments the batteries were discharged to 0.7 volt per cell on closed curcuit. Discharging down to a lower value would necessarily give a lower average voltage. The capacity of the cells shows up very much greater than the rated capacity, and this fact alone should have called Mr. Smith's attention to the lower limit of our discharge. Of the curves published by the Edison Company, some run to 1 volt, some to 0.9 volt and some lower still. We selected merely as an arbitrary standard 0.7 volt as the lowest possible limit in actual practice.

Dr. C. G. Schlaederberg: I think that the question of loss of efficiency at low temperature will perhaps bear a little further discussion. Mr. Bennett does not dwell particularly on this point. I remember a year ago the winter was very severe, and a number of users of commercial electrical vehicles complained of the loss of efficiency on account of low temperatures; they could not get the same mileage out of the vehicles as they had secured at other seasons of the year. From a practical standpoint that is a very important matter.

Mr. H. H. Smith: I will say a word in regard to the question of temperature. The Edison battery is affected rather more by the cold than the lead battery is, and among other things, that is probably due to the fact that the Edison battery is put up in metallic containers and must be separated by a certain air space, for the sake of insulation, so that radiation takes place at a more rapid rate, not only because of the fact that air is allowed to circulate between the cells, but because the electrolyte is in the metal container, which is a better conductor of heat than the ordinary rubber container of the lead cell. That partly accounts for it, and it is partly accounted for also, by the inherent characteristics of the material of which the battery is made. If the battery in a truck or pleasure car be housed in a compartment that provides excessive ventilation—free ventilation—during cold weather, the effect of cold is appreciable, but if the compartment be made commercially tight, very little trouble is experienced in

cold weather. A number of cases have been cited and published where electric trucks in the very coldest climate have been kept in operation during the cold weather with complete success. For example, in Winnipeg, the winter before last, which was a very severe winter, the trucks in that city which were equipped with the Edison battery were kept in operation when gasoline cars were absolutely helpless, and it was only because proper precautions were taken to prevent excessive currents of cold air passing around and between the cells.

Mr. C. W. Bennett: I accept Mr. Smith's criticism in all friendliness. I am very glad to have inaccuracies pointed out, if there be such, but, as has been developed in the discussion, it is certain that the difficulty has arisen through misunderstanding. The data given here cannot lay claim to an accuracy greater than 3 or 4 percent, and it is hoped that if the Edison Company have figures on energy efficiency at abnormal rates they will publish these.

Mr. W. E. Holland (*Communicated*): This paper shows every evidence of the lack of time which the authors admit they had to make the tests and prepare the paper. It is to be regretted that data are given which were not checked but were the result of single tests. Those experienced in the testing of storage batteries know that often three or four cycles of charge and discharge must be given under the same conditions before the results will assume a stable or characteristic condition.

The method employed by the authors in determining the proper amount of charge is not accurate enough for making efficiency tests, especially when the tests are not repeated over and over. The discharge voltage in several of the tests is altogether too low, showing that either the cells were not charged and discharged enough to bring them to normal operating conditions, or else there was some abnormality in regard to the condition of the electrolyte, the contact of the connectors with the cell poles, or other important detail.

A long list of papers on the Edison storage battery is cited, in spite of which the writers consider that good data on performance is meagre. The authors could not have carefully digested the literature on the subject for exceptionally complete

information and exact data on this type of storage battery have been published, especially in the paper by Holland in "The Electrician," Volume 66, pages 47 and 83 (1910). This paper was first presented before the Association of Edison Illuminating Companies at Frontenac, Thousand Islands, September 6, 1910, and was corroborated in every important respect by a paper reporting tests by the Electrical Testing Laboratories of New York, presented at the same convention. (See minutes of twenty-sixth annual meeting of Association of Edison Illuminating Companies, pages 249 and 274). A summary of results obtained by the Electrical Testing Laboratories follows:

1. Capacity Data.—Type A-6 Battery, rated at 225 ampere-hours.

	Normal	Maximum Obtainable
Ampere-hours		
Per cell, A-6 type	262	325
Per pound of cell	13.4	16.7
Per cu. in. of cell (over all)	1.03	1.27
Watts		
Per cell, A-6 type	54.5	250
Per pound of cell	2.8	12.8
Per cu. in. of cell (over all)	0.214	0.98
Watt-hours		
Per cell, A-6 type	320	394
Per pound of cell	16.4	20.2
Per cu. in. of cell (over all)	1.25	1.55

2. Efficiency Data.

Ampere-hour (current) efficiency	85%	*97%
Watt-hour (energy) efficiency	60%	*74%

* After short charges.

3. Most efficient rate of charge, amperes, A-6 type 45
4. Average volts during discharge (normal rate) 1.21
5. Drop in voltage per cell during discharge
   Total, percent 30
   During 80 to 85 percent of discharge, percent 10

The "A-6" type of cell tested by the Electrical Testing Laboratories is exactly the same in construction as the "A-8" type tested by Messrs. Bennett and Gilbert, but is a smaller size, having six positives as against eight positives of the "A-8." Its capacity and current ratings are each 75 percent of the "A-8" ratings.

The authors have misunderstood the meaning of the term "boost charge," having confused this with a hastened full charge. A boost charge is one given after a battery has been partially discharged, supplementing the normal charge. The purpose of a boost charge is to put back a comparatively large amount of energy into a battery in a short time during idleness of the vehicle at noon or while loading, thus obtaining an output considerably higher than the normal output of the battery in a day's service. Thus, in a battery which will give 100 percent capacity when charged normally, 135 percent capacity will be obtained if the normal nightly charge is supplemented during the noon hour by a boost at twice normal rate. When still shorter periods only are available the boosting rate, according to the Edison Storage Battery Company's instructions, may be increased up to four times normal-rate for fifteen minutes, or five times normal-rate for five minutes, the net increase in capacity by such boosting being very considerable in each case.

Many interesting performance data and curves have been compiled by the Edison Storage Battery Company in their research department at Orange, N. J. These have been checked and attested by various authorities and any one particularly interested in this battery would do well to apply to the manufacturers for these data.

The discussion of self discharge in the paper, page 363, is rather vague. Data on this point, from tests by the Electrical Testing Laboratories, are as follows:

Time of Standing, Hours	Fully Charged Battery, Loss, Percent	One-third Discharged Battery, Loss, Percent
1	3.5	0.5
3	5.5	1.0
6	7.0	1.5
12	8.5	1.5
24	11.0	1.5

Part of the loss of capacity on standing is explained by the cooling of the battery, resulting in lower average temperature during the discharge, as compared to the temperature when discharged immediately after charge. The remainder of the loss

is probably due, as the authors surmise, to spontaneous decomposition of the nickel peroxide.

The results obtained by the authors at low temperature are not in accord with results obtained in another series of tests by the Electrical Testing Laboratories (see "The Central Station," Dec., 1911, page 135), the true variation being considerably greater than reported by the authors. The disagreement is probably due to not enough cycles having been given in the present instance.

It is little realized what an extremely important apparatus the Edison storage battery really is, especially in its application to transportation problems. Only two things stand in the way of the universal adoption of the Edison storage battery for vehicle propulsion; namely, (1) the comparatively great variation of voltage with changes of load, due to high internal resistance, and (2) electrolytic corrosion of the steel containers of Edison cells, due to grounding by moisture. Both of these weaknesses bid fair to be eliminated in the near future by improvements contemplated by the manufacturers.

Mr. C. W. Bennett (*Communicated*): Mr. Holland has referred to some data published by him in 1910. These papers do not contain the information which it is the express purpose of this paper to give, namely—energy efficiencies under abnormal rates of charge and discharge. Mr. Holland has run the Edison cell at abnormal rates, discharging in each case down to zero voltage, completely charging without giving any data as to how much energy is put into the battery after it has been discharged at the abnormal rate, so that his material is worthless for the calculation of energy efficiencies at high operating rates. He gives the maximum efficiency obtained and the normal efficiency. It is very probable that from some range of charge and discharge, the efficiency is practically 100 percent, but this fact is worthless in itself.

The method given for determining the completion of the charge of course is not accurate, and we would be very grateful to Mr. Holland if he would give us some suggestion as to a better

method, rather than reiterating the statement that the method we submit is valueless.

In our paper, we have been careful to define just what we meant by "boost charge." No one can misunderstand what we refer to. The statement as to the loss of capacity in the battery on standing was taken from the data given by Mr. Holland in his discussion.

In regard to the statement that the batteries used had not reached normal working conditions, such a defect in the battery should be remedied in some way. If a battery is not in continuous use, which is the safe assumption for the ordinary battery, certainly if this is a factor, the maximum efficiency will not be reached. Under these conditions the maximum efficiency will be reached in practice in a few cases only. Therefore, the efficiencies obtained in our laboratory more nearly approach practical efficiencies than those obtained by the Edison Company under ideal conditions.

As a check on this work some efficiency tests have been run in our laboratory since this paper was written. Two batteries consisting of five B-4 eighty ampere-hour cells each, were used. The cells were purchased from the Edison Company and were sent to us charged ready for use. After using for a number of cycles at normal rates, efficiency tests were made. The energy efficiency of one battery was 37 percent, that of the other was 44 percent, an average of two determinations on the latter, giving 43.5 percent. The statement made by Mr. Smith and Mr. Holland that the batteries were probably not worked into condition, caused us to think that these cells should receive an overcharge. We thereupon charged the cells for twenty hours at normal rate and about twenty-four hours at half the normal rate, discharging down to our standard voltage of 0.7 volt per cell. The output of these cells with a very heavy overcharge, figuring an input of the normal rate for seven hours, as recommended by the Edison Company, gave only about 51 percent efficiency. Starting from a practically discharged cell, we then ran an energy efficiency of the two batteries, which according to the statements of the gentlemen should be under ideal conditions, for the battery had been

worked through a number of cycles and had previously received a heavy overcharge. To our astonishment, however, the efficiencies ran lower than those represented in this paper. One battery gave 51.2 percent, the other gave 49.2 percent. These measurements were made by taking readings every ten minutes as before. I have no right to assume that there is anything wrong with the cells furnished me by the Edison Company, because they were bought for new cells.

A paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 3, 1913, President W. Lash Miller in the Chair.

CONCENTRATION CHANGES IN THE ELECTROLYSIS OF COPPER SULPHATE SOLUTIONS.

By C. W. Bennett and C. O. Brown.

It has been noticed[1] that in the electrolysis of copper sulphate solutions with a rotating copper cathode the potential drop across the cell, with constant current, increases with an increase in the speed of rotation. In view of the fact that a more efficient stirring of the solution is obtained by increasing the rotation. concentration differences being thereby lessened, a drop in potential difference might be expected as a random prediction. Since this increase is rather large, and seemingly abnormal, it was deemed advisable to attempt an explanation of this phenomenon. As the object was a study of the voltage relations only, no attention was given the deposited copper except to note that it was pure, and that it completely covered the aluminum cathode upon which it was deposited.

A drawing of the cell is shown in Fig. 1, which may be described as follows: The revolving cathode, *C*, was made from a piece of aluminum pipe, 1 inch (2.5 cm.) outside diameter, and 3 in. (7.5 cm.) long. This was screwed to a brass shank which was mounted in a hollow steel spindle revolving in two bearings. The lower end of the cathode was closed with a rubber stopper. The current was led to the cathode through a wire, *E*, dipping into mercury placed in the hollow steel spindle. This cathode, mounted on an iron stand, well braced, dipped into a glass battery jar of about 1½ liters capacity. This also held the anode, *D*, of pure cast copper. The cathode was revolved by a shunt-wound D. C. motor, *G*, operating on the 110-volt circuit, with varying speeds obtained by the starting box, *H*. The current passing through the cell was taken from the same circuit

[1] Bennett: Jour. Phys. Chem., **16**, 294 (1912); Trans. Am. Electrochem. Soc., **21**, 253 (1912).

with a suitable resistance, *J*, and an ammeter, *A*, in series with the electrodes. It was at first planned to measure the back electromotive force of the cell by breaking the line circuit and instantaneously connecting a very sensitive millivoltmeter across the cell. For this purpose, a switch was designed which consisted of two double-pole switches with the blades of one removed, the switches being mounted front to front with the end

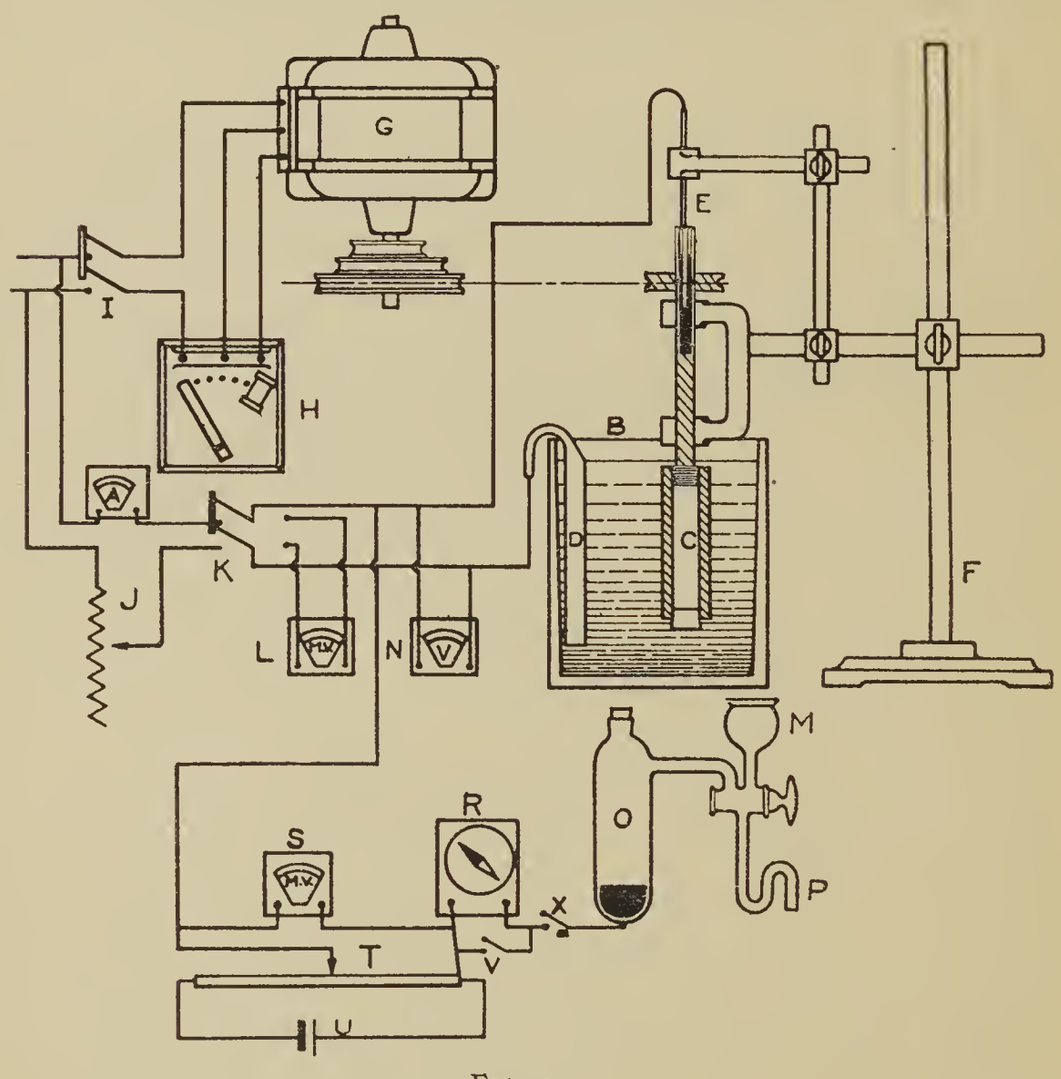

Fig. 1

terminals a few hundredths of an inch (1-2 mm.) wider apart than the width of the blade. This gave the effect of moving the end terminals of a double-throw switch very close together, so that the time for throwing the switch over was negligible. By covering this arrangement with transformer oil, the connection being the same as an ordinary double-throw switch, the line circuit could be broken even with 40 amperes flowing, and the cell connected with a delicate millivoltmeter, *L*, almost in-

stantaneously. Voltage drop across the cell was measured with a voltmeter, *N*, which was changed, whenever necessary, to insure an appropriate scale or range for the required accuracy.

It was first thought advisable to check the measurement of the rise in voltage drop mentioned above. For this measurement the solution was the same as that used in the previous investigation, consisting of a 12 per cent. solution of copper sulphate and 15 per cent. sulphuric acid. The current density as well as the speed of rotation of the cathode was varied. The results are given in Table I.

TABLE I.

Increase in Potential Difference.

Revolutions per Minute	Current Density		Amperes / Sq. Dm.	
	3.5	9.0	14.0	25.0
	Difference of Potential, Volts			
1,000	0.380	0.880	0.910	2.250
2,000	0.390	0.890	0.919	2.300
3,000	0.400	0.900	0.950	2.400
4,000	0.410	0.910	0.965	2.400
5,000	0.410	0.930	1.000	2.450

The increase with high currents is partly due to the fact that the resistance to the flow of a large current is affected relatively more than that with low currents by the air which is drawn down into the solution, the latter occurring at high speed of rotation.

The most natural assumption to make in attempting an explanation of this phenomenon is, that it is due to an increase of resistance. This resistance may be a true one, or a virtual one, of the nature of a back electromotive force. Since the latter was the most easily handled, it was studied first. This order was chosen also on account of the fact, as will be seen below, that the results obtained here would show whether or not the real resistance factor was the important one.

In order to determine whether concentration differences were important, attempts were made to measure the back electromo-

tive force of the cell directly, using the double-throw oil switch described above. A characteristic measurement may be given.

TABLE II.

Back Electromotive Force, C. D. 14 Amps./Sq. Dm.

Speed of Rotation	Back E. M. F.
1000 R. P. M.	0.018 Volt
2000 "	0.020 "
3000 "	0.021 "
4000 "	0.022 "
5000 "	0.022 "

A slight difference was obtained, but not the difference sought for, which from Table I is seen to be 0.090 volt. It was decided that the time element in throwing the switch entered in here, so that concentration changes were equalized by the rapid stirring before the meter could be connected across the cell. This method of attack was therefore not pursued further.

If the voltage rise from 1,000 to 5,000 R. P. M., as shown in Table I, be plotted against current, and the curve be extrapolated to zero current, an approximation of the real increase will be obtained, which eliminates the effect of resistance changes in the solution. This is shown by a curve in Fig. 2, obtained by plotting the values from Table I. It may be seen that this curve extrapolates back to about 0.012 volt with zero current. This would indicate that there was a counter electromotive force in the cell itself without current flowing of the order of magnitude of 10 to 15 millivolts.

The next measurement to be made, therefore, was that of the voltage of the cell

copper | acidified $CuSO_4$ solution | rotating copper electrode,

at varying speeds of rotation of the electrode, to ascertain if there was a voltage which could act as a back electromotive force. For this a delicate millivoltmeter was used. The stationary electrode was cast copper, while the copper on the revolving element was deposited there with an elevated current density and with rotation, which keeps the metal surface smooth, and is equivalent to working it cold. As has been shown[2] in the previ-

[2] *Loc. cit.*

ous investigation, the crystals are small, while those of the cast anode are larger. Fine crystals have a larger solution pressure than large[3] ones, and consequently, the electrolytic solution pressure of fine-grained copper is higher than that of coarsely crystalline copper. As a consequence, therefore, since this occurs, an electromotive force must be set up through the solution from the electrolytic copper to the cast sheet. In other words, the electrolytic copper, even when stationary, should act as anode. This has been noted in the potential[4] of rough and polished metals. In the former case there are large crystals, while in the latter, practically the so-called amorphous material only is present. With zinc a difference of about 0.32 volt, and with copper, about 0.05 volt was obtained, the polished metal becoming more electropositive and therefore showing a greater solution pressure. Actual measurement of the case above showed that the prediction was valid. This, as well as the increase in voltage with increased rotation, is shown in Table III. The solution was the same as the one used above.

TABLE III.

Voltage Increase.

Speed of Rotation	Voltage of Cell
0 R. P. M.	0.006 Volt
1000 "	0.009 "
2000 "	0.009 "
3000 "	0.010 "
4000 "	0.012 "
5600 "	0.014 "

From this it may be seen that there is an increase in the voltage of the cell with increased rotation of the anode (cathode when used as a secondary cell). In other words, this is equivalent to an increase in the back electromotive force. These measurements show that the increase in the resistance is not the important factor in determining the increase in voltage drop with rotation, when current is flowing. If it were all-important, the voltage should decrease, for the internal resistance would increase. Practically no loss due to the brush contact could be measured, so this was not considered further.

[3] Kenrick: Jour. Phys. Chem., **16**, 515 (1912).
[4] Erskine-Murray: Phil. Mag. [5] **45**, 403 (1898).

It has been shown that the effect of increased rotation is to increase the voltage of the above-named cell. The resistance of the cell may be increased, it being necessary to postulate that the voltage increases relatively faster than the resistance, giving the final effect of a rise in voltage.

In order to eliminate the effect of resistance and determine the true increase of potential due to rotation, the voltage of the rotating cathode was measured against a standard mercury electrode, using the compensation method. The electrode and bridge used are shown in Fig. 1. The electrode consisted of

Mercury, Mercurous Sulphate | 2 N sulphuric acid.

The following was obtained with the rotating electrode, 12 per cent. copper sulphate and 15 per cent. sulphuric acid solution being used.

TABLE IV.

True Increase of Potential of Rotating Electrode.

Speed of Rotation	Voltage
0 R. P. M.	0.386 Volt
1000 "	0.390 "
2000 "	0.393 "
3000 "	0.395 "
4000 "	0.397 "
5000 "	0.400 "

The increase is of the same order of magnitude as that measured by the millivoltmeter, as given in Table III, and also of the same magnitude as the rise in voltage given by the curve in Fig. 2, with zero current. It may be said, therefore, that the increase in voltage is sufficient to explain the facts as obtained from the extrapolation of the curve in Fig. 2. The increase in the effect of rotation with increased current flowing will be discussed later. No change in the potential of the stationary electrode with increasing rotation of the other, could be measured.

Having seen that the effect is caused by the increased potential of the rotating element, creating a back electromotive force, the question as to the cause of this increased potential demands attention. The increase in voltage is necessarily due to an increased solubility of the copper from the rotating element, as the rotation increases. The increased solubility of the copper in

the acid present, by the introduction of air or by the removal of the copper ions from the sphere of action, by more efficient stirring, thus making room for more, and thereby increasing the rate of solution, was shown to be incapable of explaining any rise. For this a 15 per cent. solution of sulphuric acid, with no copper sulphate, was used. The voltage was measured against the standard electrode by compensation, but practically no change with rotation was obtained. Using this as a secondary cell, and measuring the drop of potential at the revolving element (cathode) by compensation, no increase in potential difference could be detected as the speed of rotation was varied. It must, there-

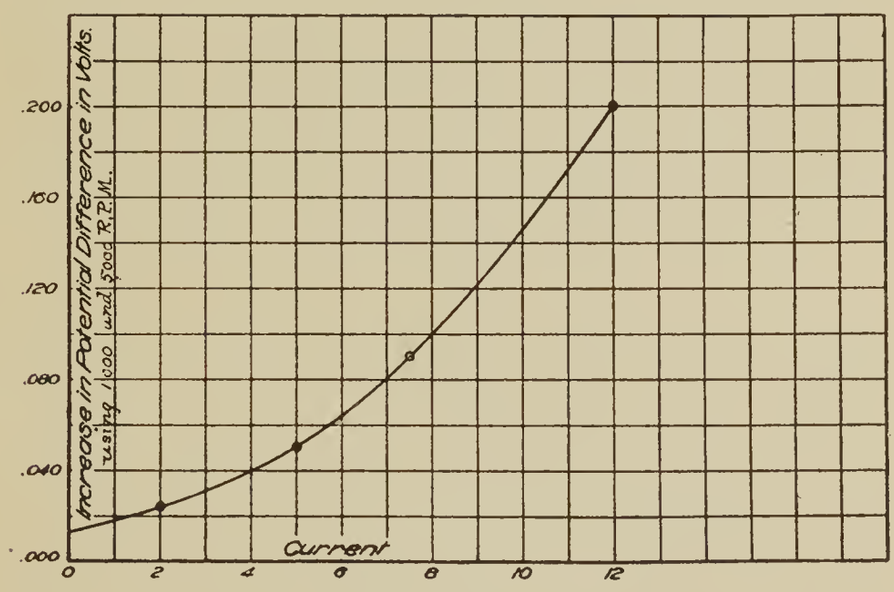

FIG. 2.

fore, be concluded that the increase in the potential must be due to a reaction between massive copper and the cupric ions in the solution. The reaction normally presenting itself is the formation of cuprous ions, thus:

$$Cu + \ddot{Cu} = 2\,\dot{Cu}$$

If it be assumed that the crystal size of the metal of the rotating electrode is constant, as it is while measuring single potentials, the solution pressure of this electrode is constant. Under these conditions the voltage of the electrode will be determined by the ratio of cuprous to cupric ions in the solution, the voltage being less the higher the ratio. If the cuprous ions are rapidly removed from the surface of the metal, the ratio will be de-

creased and therefore a higher voltage will be generated. This removal of cuprous ions is obtained by rapid stirring or rapid rotation. With a constant concentration of cupric ions, the voltage under these conditions will vary inversely with the concentration

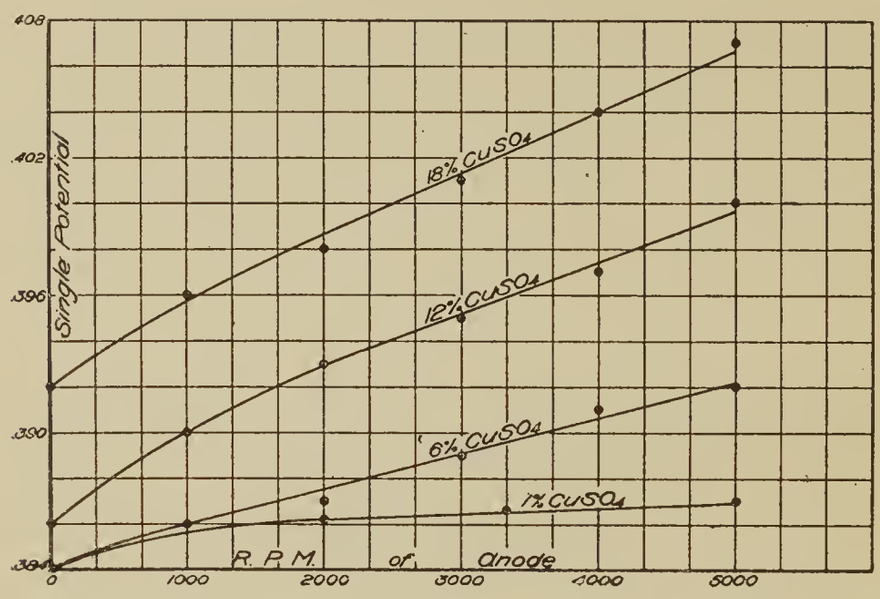

FIG. 3.

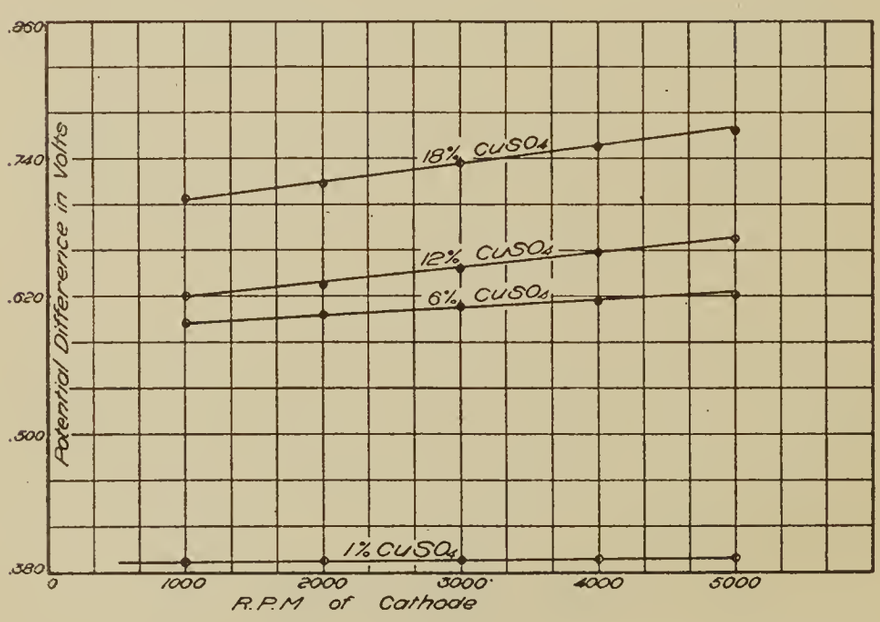

FIG. 4.

of cuprous ions in contact with the metal. The stirring increasing and hence the concentration of cuprous ions decreasing at the surface of the metal by rotation, the voltage should increase with increased rotation, as was actually found. Equilibrium conditions in the film of solution over the surface of a stationary electrode may be approximated, at least. For the sake of argument, on

the other hand, it may be assumed that with the more rapid stirring, the cuprous ions are removed as fast as formed. These two conditions represent a change of concentration of cuprous ions in the surface film over the electrode, from practically zero, to an amount depending on the equilibrium ratio of cuprous to cupric ions. This concentration difference, from what has been said above, corresponds to a definite voltage difference. Having obtained this, a prediction can be made which may allow the theory to be checked. Keeping other factors constant, if the equilibrium ratio requires a relatively small number of cuprous ions instead of a large number in equilibrium with cupric ions, the concentration difference from zero to maximum is decreased, and therefore the voltage difference would be decreased. Whether these limits can be reached actually or not is a question; the results, however, will be the same, since the limits are approached. In order to test this it is only necessary to study the voltage rise in solutions where something is known as to the concentration of cuprous relative to cupric ions, at equilibrium. In the first place, other things being equal, the concentration of cuprous ions depends on that of the cupric ions. The voltage variation with rotation, therefore, should be greater the greater the number of cupric ions, or, in other words, the stronger the solution. When this factor was varied the rise in voltage measured was that shown by the curves in Fig. 3. The slopes of the curves showing voltage differences are greater the more concentrated the solution. This same relation is shown when the cathode drop is measured, when a current is passed through the cell. This is shown by curves in Fig. 4.

Variation of the acid concentration affects the equilibrium in the same direction as the variation of the cupric ions. The voltage difference should be greater, therefore, the stronger the acid. The validity of this prediction may be seen from the curves in Fig. 5, where the acid content of a 12 per cent. copper sulphate solution is varied. The voltage difference, with increased rotation, shown by the slope of the curves, increases with increased acid concentration.

The 12 per cent. solution was run at 50° C., the increase in single potential being about one millivolt greater than at room

temperature. This difference is not large, but is in the proper direction, since an elevated temperature increases the concentration of cuprous ions in equilibrium with cupric ions.

In the copper coulometer, it is well known that alcohol decreases the concentration of cuprous ions at equilibrium. The

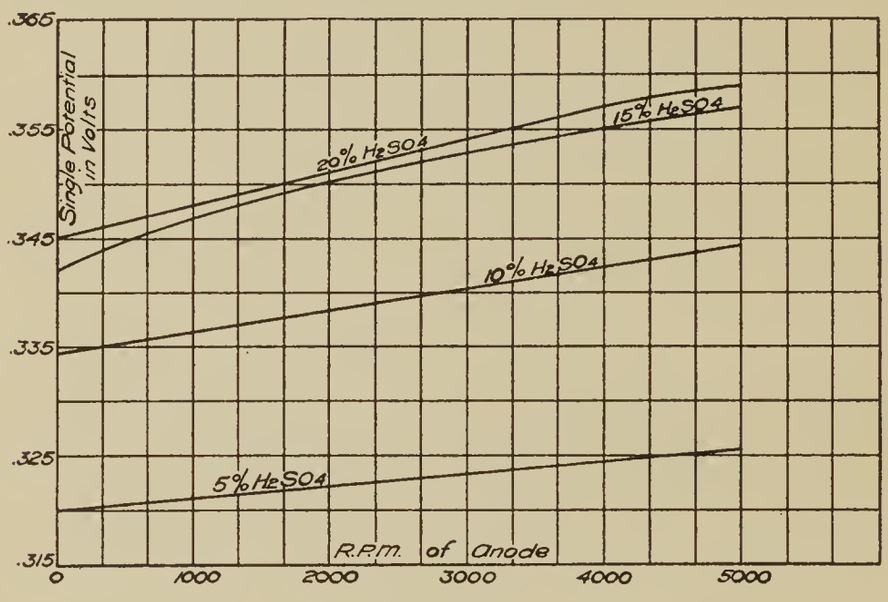

FIG. 5.

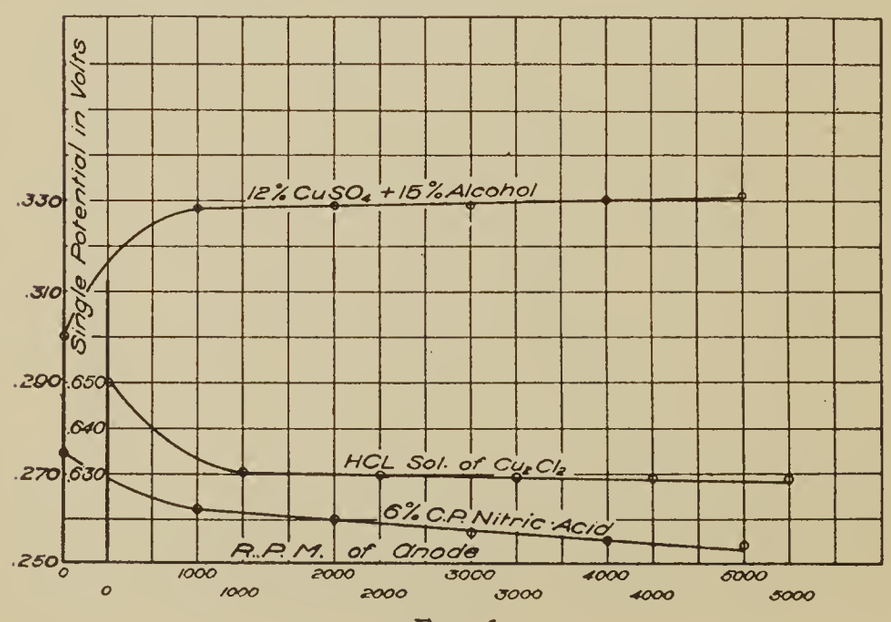

FIG. 6.

voltage difference, therefore, with increased rotation should be less when alcohol is present than when absent. With 15 per cent. alcohol in the solution the voltage rise is slight, as is shown in Fig. 6, being 0.003 volt, as compared with 0.010 for the solution without alcohol.

As a final check on the theory the potential of the rotating ele-

ment was measured in a hydrochloric acid solution of cuprous chloride. This is also shown in Fig. 6. The potential decreases markedly from stationary to 1,000 revolutions per minute and then very slightly as the rotation is increased. The explanation is simple. There is a small number of cupric ions at the electrode, in equilibrium with the cuprous ions and metallic copper. By rotating the electrode these cupric ions are removed, being replaced by undissociated cuprous salt, which may dissociate to maintain the concentration of cuprous ions. The voltage therefore decreases with rotation by an amount depending on the efficiency of removal of cupric ions from the electrode.

It has been shown recently by work[5] on the quantitative separation of copper, that the corrosion of a stationary piece of copper in nitric acid solution was many times that of a rotating piece. This is explained by considering that the rotation prevents the accumulation of nitrous acid at the surface of the copper, by reduction of the nitric acid, since it is thrown off practically as fast as formed. The nitrous acid, the active agent in dissolving copper, not being allowed to act, the metal is corroded only slowly as compared with the stationary sheet where this reagent may accumulate.

Since the solubility is decreased by rotation, the electromotive force or the potential of the metal should decrease with rotation in nitric acid solution. This was checked experimentally and found to be true. The curve is shown in Fig. 6.

It has been seen (Table I and Fig. 4) that the drop across the cell with current flowing is greater than 10 to 15 millivolts, or the value accounted for by the increased voltage of the cell in the direction opposite to the flow of the current. A part of this is unquestionably due to an increase in resistance by air bubbles as was stated above. Aside from this, however, the back electromotive force of the rotating electrode may be higher than the electrode potential measured. The current will deposit cuprous ions more easily than accomplish the reduction of cupric to cuprous ions. The concentration of cuprous ions during this electrolysis, therefore, may be considered practically negligible. Since their concentration is zero, the voltage or back electromotive

[5] Stansbie: Proc. of the Faraday Soc., Nov. 26, 1912.

force will be greater than when appreciable amounts of these ions are present, as must be the case when single potential are measured.

From this work it may be concluded that:

1. There is a definite measurable increase in potential difference in the electrolysis of acid copper sulphate solution, as the speed of rotation of the cathode is increased, from 1,000 to 5,000 R. P. M., for instance.

2. From Fig. 2, the increase indicated to maintain zero current is about 0.010 or 0.015 volt.

3. This can be accounted for by the increase in the rotating electrode potential, with increased rate of rotation.

4. The increase in the potential of the rotating electrode with increased rotation is due to the tendency to form cuprous ions, the increase being greater when conditions are favorable for the formation of cuprous ions, and *vice versa*. As the rotation increases, the stirring becomes more efficient, the cuprous ions are removed, and the solubility of the copper is therefore increased. This gives rise to a higher voltage.

5. The potential of the rotating electrode (cathode when current is flowing) may be much higher than that measured here without current, probably due to the removal of cuprous ions from the solution by precipitation.

6. The increase in the drop of potential with increasing rate of rotation of the cathode in the copper-copper sulphate electrolysis is probably due in part to an increased resistance.

7. The decrease in the potential of the electrode in cuprous chloride solution is due to the more rapid removal of the cupric ions with stirring, thus removing the reagent dissolving the copper.

8. The potential of a rotating electrode in nitric acid goes down with increasing rate of rotation, due to throwing off more and more thoroughly the film of nitrous acid, thus decreasing the solution of the copper, and therefore its voltage.

9. The solution pressure of a metal is increased if the size of its crystals be decreased. This is made apparent by an increase in the potential of the metal as the crystal size is decreased, by

hammering or burnishing, for instance. It is also shown by the fact that fine-grained metal (electrolytic copper) is electro-positive to more coarsely crystalline metal (cast copper).

Electrochemical Laboratory,
Cornell University.

DISCUSSION.

DR. W. LASH MILLER: This phenomenon of polarization, over and above what can be accounted for by concentration differences, is certainly attracting more attention than anything else from those interested in electrochemical theory.

On page 388 you describe a measurement of the voltage by the compensation method. Was the current flowing through during the measurements?

MR. C. W. BENNETT: No current was flowing.

DR. W. LASH MILLER: How long did the millivoltmeter keep the value that is given in Table I?

MR. C. W. BENNETT: The needle will not remain constant at the highest point, but gradually drops back. I should estimate that at a value slightly below the maximum the needle of the millivoltmeter will remain constant for about a minute.

DR. W. LASH MILLER: As long as that?

MR. C. W. BENNETT: At a slightly lower value than the maximum.

DR. W. LASH MILLER: As I understand it, you assume that cuprous salt diffuses away from the electrode surface out into the body of the solution, where it is oxidized by dissolved air, so that the concentration of the cuprous salt at the cathode is kept continually lower than corresponds to equilibrium between cupric salt, cuprous salt and metallic copper. Such a lowering of the concentration would undoubtedly raise the E. M. F. necessary to reduce cuprous salt to metallic copper, but at the same time it would lessen the E. M. F. needed to reduce cupric to

cuprous salt. Are you not assuming that the electrochemical reaction at the cathode results in a quantitative deposition of copper, in other words, that none of the current is employed in restoring the concentration of the cuprous salt?

Mr. C. W. Bennett: The natural assumption here, of course, is that copper is deposited as metal from the cuprous state if there are any cuprous ions present. Thus probably the concentration of cuprous ions is practically zero, made so by a deposition or reduction to the metallic state rather than oxidation back to cupric ions. The reasoning, of course, leads also to the conclusion that the reduction from cuprous ions to metallic copper takes place more easily than the reduction of cupric to cuprous ions. The oxidation by the air would correspond to depolarization, and would therefore decrease the efficiency of the deposition of copper. From experiments the efficiency is practically 100 percent, so that this depolarization is not a large factor in the sulphate solutions. So far as I know it will be practically impossible to check up these theories. They are, however, logical and, I think, fit in with the facts.

Dr. W. Lash Miller: Could is not be checked by experiments with solutions of chlorides in which (unlike the sulphate solutions) it is possible to have equal concentrations of cupric and cuprous salt? In Dushman's experiments, where copper served as anode in hydrochloric acid, he found it would dissolve practically altogether as cupric salt or altogether as cuprous salt according to conditions; all his results were in agreement with the supposition that, at the surface of the electrode, equilibrium was maintained between the two salts and the metal, while your explanation of the overvoltage is based on the assumption that the equilibrium is destroyed by diffusion.

Dr. Irving Langmuir: On page 386 the statement is made: "A slight difference was obtained, but not the difference sought for, which from Table I is seen to be 0.090 volt. It was decided that the time element in throwing the switch entered in here, so that concentration changes were equalized by the rapid stirring before the meter could be connected across the cell. This method of attack was, therefore, not pursued further." Could not the difficulty be avoided by throwing the current of this

double-throw on to a potentiometer instead of on to a millivoltmeter?

MR. C. W. BENNETT: We at first assumed that this voltage difference might be occasioned by a difference in the concentration of the copper ions at the surface of the electrodes. A certain amount of impoverishment will take place at the cathode, the rotating element. Let us say, therefore, that we will have a solution containing 5 percent copper sulphate at this electrode and a solution containing 15 percent at the stationary anode. We have copper dipping into solutions of different concentrations and therefore a concentration cell, so that we had hoped to measure the voltage generated by this concentration cell by means of the double-throw oil switch. The time element referred to here was the time required for breaking up this impoverished film over the surface of the rotating electrode by the rotation itself. Equalization of the concentration of these two solutions would therefore enter in, in the case of the potentiometer, just as in the case of the millivoltmeter. The fact that a current is being used up in the voltmeter would therefore have practically no effect, since the equalization is due to the stirring.

MR. W. C. ARSEM: I think the reason for not being able to measure that counter electromotive force by opening the switch and throwing the potential on the voltmeter may be because the voltmeter itself has a low resistance, so that in the first instant it has taken enough current to cause changes in the concentrations at the electrodes, and you do not measure the back voltage correctly. By the time the needle has come to rest the voltage may be lower because of the current which is taken by the voltmeter in the time necessary to move the meter needle.

MR. C. W. BENNETT: I tried to get a voltmeter with a high resistance, but I was informed that the Weston Company did not make the desired instrument.

DR. CARL HERING: I happen to know that the Weston Company does make such a meter.

MR. C. W. BENNETT: Not above one ohm per volt.

PROF. JOS. W. RICHARDS: As I understand, the anode was cast copper, and since the cathode, when the copper is being

deposited, is pure electrolytic copper, would there not be a difference of potential due to the different state of the copper at the electrodes? Cast copper always contains some copper oxide, and therefore the solution of copper oxide while depositing copper would require some energy expenditure which probably would represent the 6 millivolts without the rotation. Would the mechanical equivalent of the centrifugal force account for any of this increase of voltage without increased rotation? It would be in that direction, I understand, but possibly very small.

Mr. C. W. Bennett: In regard to the reference to Table III and the 6 millivolts of the cell, stationary, I would refer to the last conclusion in my paper. The electrolytic deposit becomes electropositive to the cast copper. If this voltage difference were occasioned by the presence of copper oxide in the cast metal, the cast metal would become electropositive to the electrodeposited metal. This difference in voltage is therefore not occasioned by the presence of oxide in the cast metal. We are thus reduced to the consideration of the physical state of the metal itself. In the experiments of Erskine-Murray it has been found that polished metals become electropositive to rough metals. The crystal size has been markedly decreased, and therefore the polished metals have their solubility equilibrium displaced, a higher solubility being obtained with the smaller crystals.

In regard to the last question, Prof. T. W. Richards has shown that concentration differences may be occasioned, in solutions, by centrifugal force. These concentration differences, of course, give rise to differences in electromotive force. If this factor is important the effect should be felt throughout the solution. We attempted to measure differences in voltages of the anode, but could detect practically no difference with change of rotation of cathode even though the anode was out in the solution. Since these differences are not manifest except by rotating objects, it may be assumed that they are not caused by centrifugal force. The solution does not travel with any very great speed on account of the fact that the slip between the solution and the cathode is very great. The solution is probably revolving in the cell about 500 revolutions per minute, which, you see, is negligible as compared with 10,000, which you know must be used to obtain a sufficient difference in concentration to produce an appreciable

electromotive force. The centrifugal force theory or hypothesis has not been introduced to explain these differences in voltage, which with current flowing, of course, amount to 1½ to 2 volts.

DR. CARL HERING: Was there any air sucked down around the cathode?

MR. C. W. BENNETT: Yes, and an explanation for part of the increase in the difference of potential is unquestionably caused by this, as has been noted.

DR. CARL HERING: Why not cover them with oil to prevent the air getting there? If you measure the voltage between two copper plates, and then take out the cathode and let air get at it, and put it in again, you get a different voltage. If the air comes in contact with the cathode it might make a difference in the voltage.

MR. C. W. BENNETT: This is quite true, but we measured the voltage of the anode with increasing rotation and found practically no change in this voltage. As has been said before, only when the electrode was rotated did a change occur. The use of oil to prevent drawing of air down into the solution is, I think, impractical on account of the fact that the agitation is so great that the oil itself would be emulsified.

DR. W. LASH MILLER: The effect of air is merely to oxidize the cuprous salt?

MR. C. W. BENNETT: The air, of course, would oxidize cuprous salts, if any were present. It would also increase the current density per unit of cross-section of solution, so that the potential drop would presumably be higher. This would be occasioned, of course, by the fact that the air bubbles cut down the effective area of the solution.

A paper presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 3, 1913, President W. Lash Miller in the Chair.

WATER-IMMISCIBLE ORGANIC LIQUIDS AS CENTRAL CONDUCTORS IN GALVANIC CELLS

By Reinhard Beutner.

A year ago I had the privilege of presenting a paper before this Society[1] on electromotive forces generated by systems containing immiscible electrolytic conductors. I also mentioned in that paper some investigations relating to biological applications of the electrochemical researches along this line carried out by Dr. J. Loeb and the writer, in which it had been found that the skin of plants behaves like an electrode reversible with respect to various positive ions.

As I pointed out, a phenomenon of this kind was not yet known in electrochemistry, though certain investigations of Nernst and of Haber (which were there discussed at length) had shown that a phase junction between immiscible electrolytes acts like the surface of a metallic electrode. This did not explain how such an effect was possible.[2]

More recent investigations which the writer has carried out have proved that with a number of water-immiscible organic substances similar effects can be produced as with the skin of plants. This has led to further investigations into the electromotive properties of water-immiscible organic substances, and the surprising result has been reached that cells may be built up from such organic compounds and aqueous solutions showing an electromotive force which nearly equals in magnitude the E. M. F. of galvanic cells with metallic electrodes. An explanation of these phenomena has been found possible on the basis of the well-known theories of chemical thermodynamics. The quantitative mathematical applications involved, however, many difficult questions.

[1] Beutner, Trans. Am. Electrochemical Society, **21**, 219 (1912).

[2] The explanation given, that "a chemical reaction takes place between the aqueous solution and a water-insoluble compound of the membrane causing an exchange," was hardly more than a very indefinite hypothesis, and it seems rather accidental that it is right in some degree, as we shall see later.

I. SALICYLIC ALDEHYDE AS ELECTRODE.

Nernst's law for potential differences at the junction of immiscible phases holds as follows:

$$e = \frac{RT}{nF} \ln \frac{C_1}{C_2} + \text{const.}$$

as was proved in the simplest manner possible in my previous communication. The meanings of R, T, n and F are as usual, while C_1 and C_2 are the respective concentrations of the same ion in the two immiscible phases. If one of these phases is an aqueous solution of various salts, and the second a homogeneous mixture of a great number of water-insoluble salts, we can easily understand from this formula that any of these various ions contained in the second phase influences the potential difference if it is contained in the aqueous solution in a concentration subject to arbitrary change.

The fact, however, is that chemically-pure water-immiscible substances exhibit a behavior of this kind. The best example of a substance of this character that I have been able to find so far is salicylic aldehyde, which behaves like an electrode for various cations.

In the following tables the sign of the E. M. F. is marked as + if the right side of the cell is positive.[3]

TABLE I.

Hg	$Hg_2Cl_2 \cdot \frac{m}{10} KCl$	sat. salicylic acid in salicylic aldehyde
aqueous solution variable composition	$\frac{m}{10} KCl \cdot Hg_2Cl_2$	Hg

E. M. F., using variable aqueous solutions, as follows:

Concentration (Mol. fractions per liter)	KCl E.M.F. Millivolts	Na Cl E.M.F. Millivolts	Na_2SO_4 E.M.F. Millivolts	$Ca\,Cl_2$ E.M.F. Millivolts	NH_4Cl E.M.F. Millivolts
5 m/2	— 39	..	..	..	..
m/2	— 21	..	..	..	..
m/10	0	+ 16	+16	+ 37	0
m/50	+ 24	+ 38	+32	+ 54	+24
m/250	+ 54	+ 64	+44	+ 82	+50
m/1250	+ 89	+ 90	+73	+100	+82
m/6250	+130	+124	..	+124	..

[3] These e. m. f's were measured by means of Dolezalek's electrometer. This instrument, in which the deflections are proportional to the e. m. f. applied, was standardized with the Clark standard cell. The experimental arrangement used to build up the "cell" systems was very simple, a U tube containing the salicylic aldehyde.

Concentration (Mol. fractions per liter)	$CuSO_4$ E.M.F. Millivolts	$AlCl_3$ E.M.F. Millivolts	Na Acetate E.M.F. Millivolts	H_2SO_4 E.M.F. Millivolts	$HgCl_2$ E.M.F. Millivolts
m/10	+14	+ 7	+ 64	—10	+120
m/50	+24	+32	+ 68	+20	..
m/250	+35	+52	+ 82	+56	+159
m/1250	+57	+69	+113	+83	(at m/100)

All these measurements, which were performed at room temperature, prove that the change of the E. M. F. with concentration occurs in the same direction with all salts. The point where this change takes place must be the phase junction between the salicylic aldehyde and the solution, because the change of the "liquid potential" located at the junction of the calomel electrode and the solution is too small to account for the total change observed. In the first series of measurements (with KCl solutions) there is no liquid potential difference at all; since the migration velocities of the K ions and the Cl ions are very nearly equal, and the factor $U_{K^{\cdot}} - V_{Cl'} / U_{K^{\cdot}} + V_{Cl'}$ is essential for liquid potentials, the liquid potential is practically zero. The change is in this case due to the potential difference at the phase junction exclusively.

The measurements with KCl are, therefore, most suitable for studying these new potential differences. The magnitude of the change increases as the dilution decreases and approaches the value of 41 millivolts at very low concentrations. This is the value which we should expect according to Nernst's formula if the aldehyde acts like a perfect K electrode.

$$\frac{RT}{nF} \ln 5 = 58 \log 5 = 40 \text{ millivolts}$$

This fact is very important for the theoretical explanation, as we shall see later.

The same change of the potential difference is observed with all other salts. However, the "liquid potential" interferes in these cases to some extent. The measurements are reversible as a rule,[4] except in some cases, *e. g.*, $AlCl_3$, where irreversible chemical processes interfere.

The summary of these observations is that salicylic aldehyde acts like an electrode reversible for various cations. Equi-

[4] This means that in a series of measurements with different concentrations of the same salt the potential difference comes back instantly to its previous value if the same concentration is applied again.

molecular solutions of different salts, however, do not always produce the same potential difference. This is very clearly seen from the measurements with $HgCl_2$. The system:

— Calomel electrode | salic. ald. | n/10 $HgCl_2$ | calom. elec. +

has a considerable E. M. F. (0.12 volt), which is also perfectly reversible, as the following figures show:

Time in Minutes	Solution	E.M.F. Millivolts
0	m/10 $HgCl_2$	+120
8	m/10 KCl	+ 19
15	m/10 KCl	+ 0

The last value for m/10 KCl is identical with that in the above table.

II. TOLUIDINE AS ELECTRODE.

Table II contains measurements of the E. M. F. of the system:

$$\text{Hg} \;\Big|\; \text{Hg}_2\text{Cl}_2 \,.\, \frac{\text{m}}{10}\ \text{KCl} \;\Big|\; \text{ortho-toluidine} \;\Big|$$

$$\begin{matrix}\text{aqueous solution}\\ \text{variable composition}\end{matrix} \;\Big|\; \frac{\text{m}}{10}\ \text{KCl} \,.\, \text{Hg}_2\text{Cl}_2 \;\Big|\; \text{Hg}$$

In this case the organic liquid used (ortho-toluidine) behaves like an electrode reversible with respect to anions. The E. M. F. becomes more negative with decreasing concentration.

TABLE II.

Concentration (Mol. fractions per liter)	KCl E.M.F. Millivolts	NaCl E.M.F. Millivolts	$CaCl_2$ E.M.F. Millivolts	$AlCl_3$* E.M.F. Millivolts	NoOH E.M.F. Millivolts
m/10	0	0	0	—28	—19
m/50	—19	— 22	—25	—33	—42
m/250	—49	— 55	—51	—66	—51
m/1250	—72	— 87	—85	..	—75
m/6250	—94	—109	..	..	..

*These measurements are irreversible.

Concentration (Mol. fractions per liter)	KSCN E.M.F. Millivolts	KCN E.M.F. Millivolts	KNO_3 E.M.F. Millivolts	K_4FeCy E.M.F. Millivolts	Cu_2SO_4 E.M.F. Millivolts
m/2	+156	+57	—	—	—
m/10	+129	+36	+ 60	—100	—122
m/50	+100	+14	+ 32	—113	—134
m/250	+ 64	+ 4	— 3	—126	—146
m/1250	+ 26	..	— 31	—144	—154
m/6250	— 16	..	— 71	..	..
m/31250	— 62	..	—103	..	..

Concentration (Mol. fractions per liter)	Na_2SO_4 E.M.F. Millivolts	NaF E.M.F. Millivolts	Na_2HPO_4 E.M.F. Millivolts	Other Salts E.M.F. Millivolts	E.M.F. Millivolts
m/10	—114	—100	—107	m/10 $MgSO_4$	—125
m/100	—130	—133	—125	m/10 NH_4Cl	0
m/1000	..	—137	..	m/10 $BaCl_2$	0

m/10 Toluidin hydrochloride — 23. m/50 $K_2Cr_2O_7$ + 38

These figures show that toluidine has properties with respect to the electromotive forces which are equal and opposite to those of salicylic aldehyde. The potential difference changes in the opposite direction to the concentration, and we may call the potential difference, therefore, reversible for anions. As we should expect, the chemical nature of the anion is most significant for the potential difference in this case. NaCl, KCl and $CaCl_2$ give in equi-molecular concentrations about the same potential difference, evidently because they possess the same anion, while with salicylic aldehyde KCl and $CaCl_2$ gave markedly different potential differences as a result of the reversibility for cations in this case. Salts with different anions, however, like NaF and KSCN give largely-differing potential differences with toluidine, the first a considerably negative value, the second a high positive value. If we combine these two potential differences in one system, as follows:

Cal. Electr. | m/10 NaF Sol. | toloid. | m/10 KSCN | Cal.Electr.+

an E. M. F. of 0.23 volt is produced.

Other anions which give a positive potential difference at the same concentration are NO_3' and CN'', while SO_4'', $Fe(CN)_6''''$, C_2H_3O' and POH'' give a "negative" value. It may be remembered that with all these figures the Cl' is taken as arbitrary zero, as the calomel electrode used was filled with m/10 KCl solution, and this solution constantly remained in contact with the toluidine on the one side.

The rule that the chemical nature of the anion determines the potential difference at the toluidine is not without exceptions. Thus, for instance, $AlCl_3$ in a 1/10 molecular concentration exhibits a negative value distinctly different from that of KCl, NaCl, $CaCl_2$; it is found, however, that the potential difference undergoes irreversible changes with the concentration, and there are, therefore, most likely irreversible chemical processes which cause this exceptional behavior.

The figures show very clearly that the direction of the change of the potential difference is the same with all salts; it is observed, however, that with salts which even at comparatively high concentrations exhibit a "negative difference," as fluorides, sulphates, etc., the potential difference becomes only slightly more negative with diminishing concentration. The reason is evidently that in these cases the presence of even the slightest trace of salt with a higher positive potential difference interferes; if, for instance, the distilled water which is used to dilute the solution of the sulphate contains the slightest trace of a chloride, the potential difference can apparently not become more negative than corresponds to this very small chloride concentration. Considering that the chloride potential difference is much more positive, we understand why a small Cl′ concentration interferes with the SO_4'' potential difference.

The influence of the concentration upon the potential difference can for this reason be studied over a large range only with such salts as have a high positive potential difference, like KSCN; these measurements show in a very striking way how very regular and easily reproducible the change of the potential difference is. The change is larger at small concentrations, and approaches at very small concentrations the value of about 40 millivolts for a five-fold dilution. This should be expected from Nernst's formula, if the toluidine acted like a perfect SCN′ electrode (or if the SCN′ concentration in the toluidine were constant).

III. EXPERIMENTS WITH MIXTURES OF TOLUIDINE AND SALICYLIC ACID WHICH EXPLAIN THE NATURE OF THE E. M. F. DESCRIBED ABOVE.

Toluidine has a marked basic character, while salicylic acid contained in the salicylic aldehyde is a strong acid.[5] It is evident that the opposite change of the potential difference with the concentration in the two cases has something to do with the basic and with the acid character of the compounds used.

I have performed a large number of experiments with other compounds immiscible with water. Such substances as amyalcohol, benzyl alcohol, phenol, ortho-kresol or Beta-naphthol,

[5] Ostwald's "Affinitäts Konstante" has the high value of 0.102 for salicylic acid.

which do not possess a marked acid or basic function, exhibit either a very small change of the potential difference (with KCl solutions) or none at all. Bases, such as aniline, methylaniline, naphtylamine, act like toluidine; or if we dissolve a water-insoluble acid like salicylic acid in phenol or kresol, an electromotive effect similar to that of the salicylic aldehyde (which always contains salicylic acid) is produced.[6]

I have also measured the potential difference with benzaldehyde instead of salicylic aldehyde; this aldehyde naturally contains benzoic acid through oxidation with atmospheric oxygen; a similar electromotive effect to that with salicylic aldehyde is therefore observed, but the change of the potential difference with the concentration is much smaller, apparently owing to the weaker acid nature of benzoic acid as compared with that of salicylic aldehyde.

There can be no doubt, therefore, that the degree of the acid or basic properties of the water-immiscible substances is responsible for the potential differences described. The question now arises how that fact can be explained from a theoretical standpoint.

Though probably a great many explanations may be possible, only those now appear satisfactory which are based on purely thermodynamic considerations, and we therefore make Nernst's formula for phase junctions the starting point of our theory.[7] Such conceptions as, for instance, ionic permeability,[8] though still often used by some investigators, are not really based on thermodynamics, and, moreover, are found to be contradictory to observations.

Measurements of the potential difference with mixtures of toluidine and salicylic acid have served to find a satisfactory explanation. Equi-molecular parts of salicylic acid and toluidine were dissolved in ortho-kresol, and the potential differences measured with various salt solutions. No considerable change

[6] Beutner. Journal of the Am. Chem. Soc., **35**, 344 (1913).

[7] Page 402.

[8] The conception of "selective ionic permeability" was originated by Ostwald in 1890 (Zeit. phys. Chem., **6**, 11). Though it was proved to be contradictory to facts by very conclusive experiments of Tammann in 1891 (Göttinger Nachichten, **6**, 213), this conception was introduced into electrophysiology by Bernstein and adopted by many authors in that field. Freundlich some time ago introduced the conception that potential differences may be produced by "Ionic Absorption", which was also adopted by some electrophysiological authors; in a more recent publication, however, Freundlich admits, himself, that this principle fails to give a satisfactory explanation of electro-endosmotic experiments (Freundlich and Elissahoff, Zeit. phys. Chem., **79**, 385).

of the potential differences with the concentration is observed if the electrolyte dissolved in the aqueous solution is a neutral inorganic salt, as the following measurements with KCl solutions prove:

TABLE III.

Concentration of KCl sol.	E.M.F. millivolts
m/10	—5
m/100	—3
m/1000	+1

This is what we should expect on account of the fact that toluidine and salicylic acid (in the aldehyde) cause inverse effects.

The toluidine-salicylic acid mixture in the kresol contains toluidine cations and salicylic acid anions in a constant concentration. A "reversibility" for cations should therefore be observed if toluidine chloride is the electrolyte of the aqueous solutions, a reversibility for anions, on the other hand, with sodium salicylate. In the first case the ion common to both phases (kresol and water) is the toluidine cation; as the kresol concentration of it is kept constant, Nernst's formula for phase junctions provides a change of the potential difference in the same direction as at a metallic electrode if the aqueous concentration is changed. In the second case the salicylic acid anion is common to both phases, and the change of the potential difference should therefore take place in the opposite direction.

The following experiments prove that this is really the case, within a certain range of concentrations.

TABLE IV.

Hg	$Hg_2Cl_2 \cdot \frac{m}{10}$ KCl	equimolecular solution of salicylic acid and o-toluidine in o-kresol		
	aqueous solution variable composition	$\frac{m}{10}$ KCl $\cdot$ Hg_2Cl_2	Hg	

Toluidine Chloride Solution			Sodium Salicylate Solution	
Concentration	E.M.F. Millivolts		E.M.F. Millivolts	
m/2	—58	E. M. F. increasing with decreasing concentration	+53	E. M. F. decreasing with decreasing concentration
m/10	—27		+20	
m/50	— 9		+ 2	

The fact that the change is not quite as large as at metallic electrodes (40 m. v.) can be explained, first, by the solubility of toluidine salicylate in water, and, second, by the solubility of toluidine chloride and sodium salicylate in kresol. Only in case these solubilities would be practically zero, which apparently is not the case, could the value of 40 m. v. be expected.

A change of the potential difference under such conditions is observed in the same respective directions if, instead of toluidine chloride in the aqueous solution, aniline chloride or methylaniline chloride is used, or if, instead of sodium salicylate, sodium benzoate or acetate is used:

TABLE V.

Hg	$Hg_2Cl_2 \cdot \frac{m}{10}$ KCl	equimolecular solution of salicylic acid and o-toluidine in o-kresol
aqueous solution variable composition	$\frac{m}{10}$ KCl $\cdot$ Hg_2Cl_2	Hg

Concentration (Molecular Fractions per liter)	Aniline Chloride Solution E.M.F. (m..v)	Methylaniline Chloride Solution E.M.F (m.v.)	Sodium Benzoate Solution E.M.F. (m.v.)	Sodium Acetate Solution E.M.F. (m.v.)
m/2	—50	—52	+58	+41
m/10	—25	—36	+20	+17
m/50	— 6	—14	+ 4	+ 6

These figures show that a reversibility with respect to the various ions (anions or cations) is also exhibited by the toluidine-salicylic acid mixture. *The "organic" ion of the salt in the aqueous solutions determines the direction of the change;* salts with "organic" cations produce a reversibility with respect to cations, salts with "organic" anions a reversibility with respect to anions.

The explanation which seems to me most likely to account for these phenomena is based upon the assumption that a chemical reaction takes place between the electrolytes of the kresol and the water, and that the products formed by this reaction have in equilibrium a different distribution between the two solvents.

In connection with Nernst's formula this can explain the observation, for instance, with the potential difference:

toluidine salicylate in o-kresol	aniline chloride in water

as follows: Aniline chloride is soluble to some extent in kresol and toluidine salicylate in water. In both solvents, therefore, in the vicinity of the phase junction the following reaction may take place:

Toluidine salicylate + aniline chloride =
toluidine chloride + aniline salicylate.

If we assume that the aniline salicylate is more soluble in the kresol than the toluidine chloride, the effect of this exchange will be such that the aniline cations concentrate in the kresol, or, in other words, the concentration of aniline ions in the kresol does not change as the concentration of the aniline ions in the water, but is either constant and independent of the aqueous concentration of aniline cations or changes at least at a smaller rate. The aqueous concentration of aniline cations is due only to the dissociation of aniline chloride, while in the kresol both aniline salicylate and aniline chloride produce such cations. If the kresol concentration of the aniline salicylate was constant and much larger than the concentration of aniline chloride, the phase junction apparently would exhibit the maximum change of the potential difference (40 millivolts for a 5-fold dilution), because the concentration of the aniline cations in the kresol would thus be constant. Nernst's formula for phase junctions, which in this case can be applied as follows:

$$e = \frac{RT}{F} \log \frac{C \text{ aniline in water}}{C \text{ aniline in kresol}} + \text{const.}$$

would be therefore

$$e = \frac{RT}{F} \log C \text{ aniline in water} + \text{const.}$$

If the aqueous concentration is changed 1 to 5, the change of the potential difference, e, would be 40. This condition is not

quantitatively fulfilled, but a smaller change of the potential difference in the direction predicted by the theory is observed.

In an analogous way the change of the potential difference:

toluidine salicylate in o-kresol	sodium acetate in water

may be explained; the reaction which takes place in this case is:

Toluidine salicylate + sodium acetate =
toluidine acetate + sodium salicylate.

The "merely organic" salt, toluidine acetate, is more soluble in kresol, therefore the acetate anions aggregate in the kresol. The potential difference is determined in this case by the formula:

$$e = \frac{RT}{F} \log \frac{C \text{ acetate in water}}{C \text{ acetate in kresol}} + \text{const.}$$

As "C acetate in kresol" is constant, or at least does not change proportionally to "C acetate in water," the potential difference e must vary in a reversible way with respect to anions, that is, in a direction opposite to that with aniline chloride as aqueous electrolyte.

We can also explain the action of a neutral salt like NaCl in this way; the reaction would be in this case:

Toluidine salicylate + NaCl =
toluidine chloride + sodium salicylate.

Both products of the reaction are "half-organic" salts, and neither $Na^{\cdot}$ or Cl' can aggregate therefore in the kresol: the potential difference must be independent of the concentration, as was really observed.

Finally, we will discuss the action of such a salt as aniline acetate. In this case our theory would seem to predict the following. The reaction would be:

Toluidine salicylate + aniline acetate =
aniline salicylate + toluidine acetate.

In this case also both salts are distributed between kresol and water at equal rates, as they are both soluble in kresol according

to our previous assumption. The potential difference, therefore, should be independent of the concentration. This was confirmed by experiment, as the following figures show:

TABLE VI.

Aniline Acetate Solution.

(Same System as Table V.)

Concentration	E.M.F. Millivolts
m/2	—9
m/10	—4
m/50	—2

These theoretical explanations are incomplete owing to their qualitative character, since the distribution of the various salts is not known numerically; the writer has not yet been able to make such quantitative measurements. I wish to mention one qualitative experiment only, which shows the difference in distribution of aniline chloride and aniline acetate between water and kresol. If we shake an aqueous solution of aniline acetate with kresol, no aniline can be precipitated by KOH, which shows that the aniline has been taken up by the kresol; with an aqueous solution of aniline chloride, however, the aniline stays in the water after shaking with kresol under the same conditions, and can be identified by precipitation with KOH.

This theory may be applied to the electromotive forces generated by salicylic aldehyde or toluidine as follows: We take as an example the potential difference between salicylic aldehyde (saturated with salicylic acid) and KCl in aqueous solution.

The following reaction would take place in this case:

$$C_6H_4.OH.COOH + KCl = C_6H_4.OH.COOK + HCl$$

This reaction is very incomplete, *i. e.,* only very small amounts of $C_6H_4.OH.COOK$ and HCl are formed, but the $C_6H_4.OH.COOK$ is more soluble in the salicylic aldehyde, and, as KCl is present in the salicylic aldehyde in minimal traces only, the concentration of K ions in the aldehyde is chiefly due to $C_6H_4.OH.COOK$. This means that the concentrations of K ions in water and in the aldehyde are not proportional. Thus it is explained why the potential difference is reversible for cations. With a basic

substance such as toluidine the opposite effect can be explained in the same way; the reaction may be in this case:[9]

$$C_6H_4.CH_3.NH_3OH + KCl = KOH + C_6H_4.CH_3.NH_3Cl.$$

$CH_4.CH_3.NH_3Cl$ formed in traces only aggregates in the toluidine, thus making the concentration of Cl ions in toluidine independent of the concentration of Cl ions in the aqueous solution. Evidently in this way the fact is explained that any cation affects the potential difference with salicylic aldehyde and any anion with toluidine. It is just this observation which appears strange at first and hard to explain from a theoretical standpoint.

As the relation between concentration and potential difference can be examined by experiment with a sufficient accuracy over a considerable range, I have also tried a quantitative application of my theory. A mathematical development appeared possible by means of the laws of distribution and of mass-action and the assumption that the concentration of H ions and the total concentration of salicylic acid in the salicylic aldehyde remained constant. A full account of this theory will be published later;[10] it is remarkable that the larger variation of the potential difference at low concentration can be fully accounted for by this theory; as an example I wish to give here the values calculated for the change of the potential difference between toluidine and KSCN solution and compare them with the observed values:

TABLE VII.

Change of Concentration		Change of E. M. F. Calculated	Observed
From 5/2	to 1/2m	19	26 (?)
" 1/2	" 1/10m	21	27
" 1/10	" 1/50m	27	30
" 1/50	" 1/250m	34	35
" 1/250	" 1/1250m	38	37
" 1/1250	" 1/6250m	40	42
" 1/6250	" 1/31250m	40	42

IV. ELECTROMOTIVE FORCES DUE TO CHEMICAL REACTION.

The E. M. F. of systems which are mere concentration cells, as those described above, is limited, since the range over which the concentration can be varied is limited. With toluidine as an

[9] The formation of the compound $C_7H_8.NH_3.OH$ from $C_7H_8.NH_2$ and H_2O is analogous to the formation of NH_4OH.

[10] Zeitschr. f. Electrochemie., 19, 1913.

electrode and KSCN as an aqueous electrolyte, for instance, the concentration could not be increased beyond m/2, because irreversible changes of the E. M. F. (due apparently to more complicated chemical changes) interfered in more concentrated solutions; neither could the concentration be decreased beyond m/31,250, because very irregular and rapidly varying changes of the E. M. F. were observed. With such low concentrations traces of other ions apparently interfere. Further, the total range over which the E. M. F. can be varied reversibly does not exceed 0.18 volt. With other systems the range was, as a rule, considerably smaller. As was said above, larger E. M. F.s can be produced easily by systems which contain solutions of different salts, for instance by the following system:

$$- \text{Hg} \mid \text{Hg}_2\text{Cl}_2 \cdot \frac{m}{10}\text{KCl} \mid \frac{m}{10}\text{NaF} \mid \text{Toluidine} \mid$$

$$\frac{m}{10}\text{NaSCN} \mid \frac{m}{10}\text{KCl} \cdot \text{Hg}_2\text{Cl}_2 \mid \text{Hg} +$$

The E. M. F. is 0.23 volt.

While the E. M. F. of a concentration cell is due to merely physical equilibrium of two different concentrations, according to the well-known thermodynamic principles, the E. M. F. of a system like that just mentioned is apparently caused by a chemical reaction.

The question presents itself how this reaction can be determined for a definite cell system. A solution is found if we make use of the principles which we have explained in the first part of my previous paper[11] concerning the calculation of the E. M. F.s of cells formed of solid salts.

As an example, I wish to discuss the last cell system. According to the previous explanations the toluidine contains toluidine fluoride in the region where it is in contact with the NaF solution, and it contains toluidine sulfocyanate in the region where it is in contact with NaSCN solution. A system of this kind is, therefore, analogous to the cell

$$- \text{Ag} \mid \text{solid AgCl} \mid \text{solid Na}_2\text{SO}_4 \mid \text{solid Ag}_2\text{SO}_4 \mid \text{Ag} +$$

discussed in the previous paper,[11] in the following respects:

[11] Trans. Amer. Electrochem. Soc., 21, 214 (1912).

1. Both systems are built up from four electrolytes containing two cations and two anions:

(1) AgCl, NaCl, Na_2SO_4, Ag_2SO_4.

(2) NaF, Toluidine HF, Toluidine HSCN, KSCN.

2. The metallic electrodes are in both cases without influence upon the E. M. F.

3. Both systems have electromotive forces at the junction of electrolytic phases.

The "toluidine" cell contains one phase junction less than the cell with the Ag salts; it can be proved, however, that this is without influence.

It was proved (*l. c.*) that the reaction is for the Ag cell:

$$(\text{solid})Ag_2SO_4 + 2(\text{solid})NaCl = 2(\text{solid})AgCl + (\text{solid})Na_2SO_4.$$

By analogy we find for the toluidine cell:

NaSCN (in water) + toluidine fluoride (in toluidine) = toluidine sulfocyanate (in toluidine) + NaF (in water).

It must be said, however, that it is not possible to calculate the magnitude or even the direction of the E. M. F. of the toluidine cell from these considerations, since the concentration of the toluidine salts in the toluidine is entirely unknown. Besides, the thermal data have not been determined.

Considerable E. M. F. can also be produced by a system combining toluidine and salicylic aldehyde; for instance, a double concentration cell:

$$Hg \,\Big|\, Hg_2Cl_2 \cdot \frac{m}{10} KCl \,\Big|\, \text{Salicylic aldehyde} \,\Big|\, \frac{m}{1250} KCl \,\Big|\, \text{toluidine} \,\Big|\, \frac{m}{10} KCl \cdot Hg_2Cl_2 \,\Big|\, Hg$$

the E. M. F. of which is 0.19 volt, or:

$$Hg \,\Big|\, Hg_2Cl_2 \cdot \frac{m}{10} KCl \,\Big|\, \frac{m}{10} KSCN \,\Big|\, \text{toluidine} \,\Big|\, \frac{m}{10} Mg\,SO_4 \,\Big|\, \begin{matrix}\text{Salicylic}\\ \text{aldehyde}\end{matrix} \,\Big|\, \frac{m}{10} KSCN \,\Big|\, \frac{m}{10} KCl \cdot Hg_2Cl_2 \,\Big|\, Hg$$

the E. M. F. of which is 0.34 volt.

V. SOME MEASUREMENTS OF THE E. M. F. OF SYSTEMS CONTAINING VARIOUS IMMISCIBLE ORGANIC LIQUIDS AS CENTRAL CONDUCTORS.

As was said above, the potential differences at "toluidine electrodes" can be imitated with various other water-immiscible organic bases. I wish to give here some measurements of this kind.

Table VIII.

$$\text{Hg} \;\Big|\; \text{Hg}_2\text{Cl}_2 \cdot \frac{m}{10}\,\text{KCl} \;\Big|\; \text{Central Conductor} \;\Big|$$

$$\text{variable aqueous solution} \;\Big|\; \frac{m}{10}\,\text{KCl} \cdot \text{Hg}_2\text{Cl}_2 \;\Big|\; \text{Hg}$$

(1) Central Conductor: Aniline.

Variable solution NaCl	E. M. F. Millivolts	Variable solution KCL	E. M. F. Millivolts
m/10	0	m/10	0
m/100	—21	m/100	—18
m/1000	—40	m/1000	—44

(2) Central Conductor: Mixture of 5 vol. α-Napthylamine and 2 vol. Aniline.

Variable solution	E. M. F. Millivolts	Variable solution	E. M. F. Millivolts
m/10 NaCl	0	m/10 KCl	0
m/100 NaCl	—23	m/100 KCl	—39
m/1000 NaCl	—71	m/1000 KCl	—79

(3) Central Conductor: Monomethylaniline.

Variable solution KCl	E. M. F. Millivolts	Variable solution KSCN	E. M. F. Millivolts
m/10	0	m/10	+151
m/50	—22	m/50	+118
m/250	—46	m/250	+ 85

(4) Central Conductor: Xylidine.

Variable solution KCl	E. M. F. Millivolts
m/10	0
m/250	—31
m/1250	—56

The measurements given in (3) show that the peculiar effect of SCN ions which was observed with toluidine is also produced with methylaniline. It seemed worth while to examine the effect of a sulfocyanate (causing a high potential) and of sulphates (causing a negative potential) with various bases. It may be remembered, again, that m/10 KCl is the arbitrary zero with all measurements.

TABLE IX.

(System same as Table VIII.)

(1) Methylaniline.

Concentration	E. M. F. Millivolts
m/1 $MgSO_4$	— 40
m/10 KSCN	+145

(2) Xylidine.

m/10 KSCN	+124
m/10 Na_2SO_4	— 69
m/10 $MgSO_4$	— 92

(3) Aniline.

Concentration	E. M. F. Millivolts
m/10 KSCN	+ 84
m/10 Na_2SO_4	—141
m/10$MgSO_4$	—137

(4) Napthylamine and 1/10 vol. Toluidine.

m/10 KSCN	+123
m/10 Na_2SO_4	— 78

These data show that the sulfocyanates and sulphates act in the same way with all bases; the potential differences are, however, somewhat different in the different cases.

The question presented itself whether effects similar to those obtained with aromatic bases and aldehydes could also be produced with fatty compounds.

The alkyl substituted N-compounds are mostly miscible with water, and so are the lower fatty aldehydes.

As a water-immiscible fatty substance, the compound $CH_3.(CH_2)_5.C–OH$, the so-called oenanthic aldehyde, which is easily obtainable, was used. The aldehyde apparently contains a higher fatty acid due to oxidation, but no concentration effect similar to that of salicylic aldehyde could be produced, as the following figures show:

TABLE X.

Oenanthic Aldehyde.

Variable solution	E. M. F. (millivolts)
m/10 KCl	0
m/50 KCl	—17
m/250 KCl	—31
m/1250 KCl	—17

As is seen, the potential difference varies in opposite direction to that with salicylic aldehyde from m/10 to m/250, but when the concentration is decreased still further the potential difference becomes more positive. Such a peculiar change of the potential difference in two directions was observed with a number of other substances, *e. g.*, phenol or benzaldehyde, if the aqueous electrolyte used was HCl. The explanation of this phenomenon seems to be rather difficult.

I wish to give here also my measurements with esters of lower fatty acids and alcohols.

TABLE XI.

Concentration KCl	Methyl Acetate E.M.F.(m.v.)	Ethyl Acetate E.M.F.(m.v.)	Butyl Acetate E.M.F.(m.v.)
m/2	..	..	—24
m/10	0	0	0
m/50	..	+10	+29
m/250	..	+31	+60
m/1250	0	+50	+79

In the two last series of measurements the reversibility was unsatisfactory; the potential difference underwent irregular changes when the concentration of KCl was decreased, starting from m/2 concentration.

It is remarkable that the change of potential difference is larger with the higher esters, probably owing to the increasing immiscibility with water.

The following measurements with ethyl and amyl ester showed a fair reversibility:

TABLE XII.

Concentration of KCl	Ethyl Butyrate E.M.F(m.v.)	Ethyl Valerate E.M.F.(m.v.)	Amyl Acetate E.M.F.(m.v.)	Aceto-acetic Ester E.M.F.(m.v.)
5 m/2	..	..	..	—12
m/2	..	..	..	— 6
m/10	0	..	+ 1	0
m/50	+18	+ 4	— 1	+11
m/250	+38	+42	+36	+28
m/1250	+66	+88	+52	+52
m/6250	..	..	..	+76

It is seen from these measurements that the potential difference at the junction of esters and KCl solutions becomes more positive with decreasing concentration; the change is greater and more perfectly reversible with the esters which contain a great number of C-atoms.

As proved above, the acid contained in the second phase is mainly responsible for the change of the potential difference in this direction. One can conclude that the acid which is always contained in the esters (being formed through saponification) causes the effect in the last cases. This is also seen from the fact that benzonitrile, $C_6H_5.CN$, a substance of very different constitution, acts also as an electrode for various cations, the change of the potential difference being in the same direction. Apparently the benzoic acid formed by saponification is the cause. The following measurements with benzonitrile prove this:

TABLE XIII.

Benzonitrile.

Concentration	E. M. F. (m.v.)
m/10 KCl	0
m/50 KCl	+34
m/250 KCl	+65
m/1250 KCl	+84

It was also found that the changes of potential were greater when the benzonitrile had been allowed to be in contact with water for some hours, thus producing a larger amount of benzoic acid.

The theoretical explanation would seem to be the same as with salicylic aldehyde in all cases. However, the reversibility is not always satisfactory, as was mentioned. We can only guess which circumstances cause the irreversibility (*e. g.*, with methyl acetate); there may be a formation of unstable compounds in the boundary regions which interferes.

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DISCUSSION.

Dr. W. Lash Miller: The thermodynamic theory of chemical cells can be developed in its completeness only if we are certain of exactly what changes take place when the current passes; in such cases as these it must be next to impossible to actually determine that correctly; so we must congratulate Dr. Beutner on the indirect but ingenious method he has adopted for checking assumptions which it would be hard to prove directly.

On page 404 the words "perfectly reversible" are used. Does this mean anything more than that the electromotive force took quickly a definite value?

Dr. Reinhard Beutner: The electromotive force changed quickly and instantly in all these cases. In fact, the change of the potential difference of these cells is much more rapid than it would be if a metallic electrode was used.

Dr. W. Lash Miller: And on page 414, where the word "irreversible" is used, does that mean it was difficult to get definite readings?

Dr. Reinhard Beutner: That means that if I go back to the same concentration I had before I do not get the same potential difference again. All the rest of the measurements, however, are perfectly reversible, *i. e.*, if we start with the end cell solutions and go back to the first solution, we are sure to get exactly the same potential difference again.

An Experimental Lecture presented at the Twenty-third General Meeting of the American Electrochemical Society, at Atlantic City, N. J., April 4, 1913, President W. Lash Miller in the Chair.

HYPERBASIS.

LECTURE EXPERIMENTS ON SUPERSATURATION, SUPERCOOLING AND SUPERHEATING.

By Frank B. Kenrick.

The importance of hyperbasis *(Ueberschreitungserscheinungen)* in bringing about thermodynamically "improbable" reactions at the electrodes is now generally recognized, and at the request of the Board of Directors of the Society the illustrated lecture at the present meeting is devoted to this subject. It is hoped that the following notes may make it easy for those who are interested to repeat some of the experiments shown.

APPARATUS.

1. *Projection Cell.* Although lantern cells ("hollow slides") may be obtained commercially, they are often of the wrong shape or size for some special experiment. Moreover, many cells on the market will not stand rapid changes of temperature. The cell described below is free from this objection, and can be easily made or modified in a few minutes.

A glass rod is bent into a U and covered with a rubber tube (*A,* Fig. 1). Near the shorter arm is a second rod, *B,* also covered with rubber tubing. These are clamped, as shown, between two glass plates by means of four strips of wood (1.5 cm. square), *C* and *D,* bolted together at the ends. Hot or cold water, or both, may be led through the tubes, *E* and *F,* the overflow running down between *A* and *B* and being caught in the rectangular tin tray, *G,* on which the lower pair of wooden strips rest and which serves as a stand for the cell. This cell may be made double (see Exp. IV) by clamping, between the same wooden strips, a duplicate cell, in the reverse position, to the right of the cell shown in the diagram. The overflows are thus both on the outside, and do not take up valuable space in the

field of view. If thick glass (⅛-inch) is used, boiling and cold water may be led in alternately without fear of cracking. In the double cell, however, it is safer to use separate glass plates for each half of the cell.

2. *Projection Thermometer.* It may not be generally known that the mercury thread in the capillary of an ordinary milk glass thermometer shows plainly on the screen if the outer protecting tube and scale are removed and the capillary is immersed in water. A lantern thermometer can be prepared in the follow-

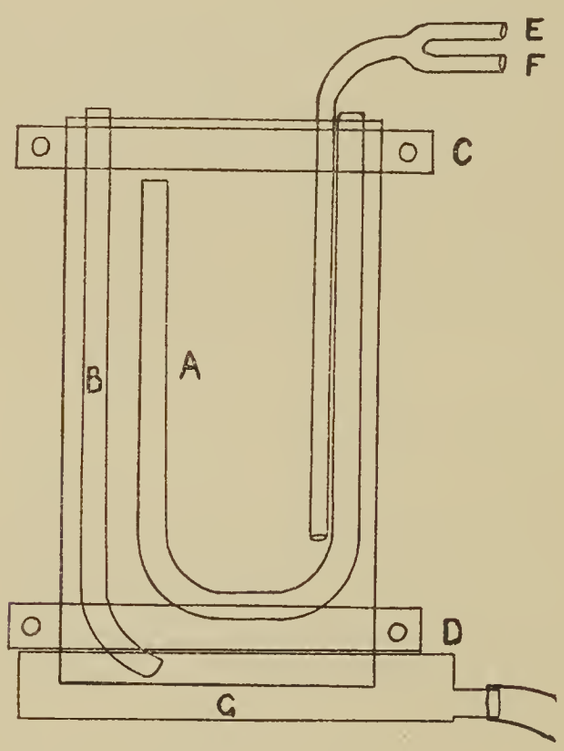

Fig. 1.

Fig. 2.

ing manner, and may be used in the cells described in (1) without monopolising too much of the limited space. The outer tube of an ordinary thermometer (—10° to 360°) is cut off as near the bulb as possible. After cutting off the tip, the capillary is bent back on itself as shown in Fig. 2. The bulb is then warmed with a Bunsen flame, while the tip of the tube is dipping in a vessel of clean mercury. As soon as the mercury column joins the mercury in the vessel the bulb is allowed to cool so as to fill the tube with mercury. The bulb is next warmed in melted paraffin to about 130° to get rid of the excess of mercury, and is finally cooled until the end of the thread has receded a few

centimeters from the tip of tube, whereupon the end is sealed up. This will bring the 100° and 0° marks into the field of view of the lantern. The small quantity of air left in the tube prevents a breaking of the hanging column of mercury. For the scale, a strip of window glass may be etched with hydrofluoric acid and attached to the capillary by cork wedges bound with thread. To economize space, a piece may be cut out of the side of the scale to make room for the thermometer bulb.

3. *Time Measurement.* A very convenient way of indicating time in fractions of a minute is to attach a small plane mirror, about 1 cm. in diameter, to the second-hand of a cheap alarm clock. The clock is held in a retort stand a foot or two behind, and to the side of, the lantern, so that a beam of light from a hole in the side of the lantern house may be reflected back from another mirror to the small mirror on the clock. If the plane of the small mirror is not exactly at right angles to the axis of rotation a spot of light will travel in a circle on the screen, and may be so adjusted that it runs round just outside the illuminated field. The "clock face" may be made either with pieces of paper pinned on the screen, or, if too much of the field is not taken up with apparatus, by the projection of an etched glass plate. To allow easy adjustment, the small mirror may be stuck to a cork impaled on a wire soldered to the second-hand, and bent at right angles to the axis.

4. *Second Pendulum.* A simple metronome for beating seconds can be made from a metal rod four or five inches long, through the middle of which is soldered a stiff wire, the ends of which are pointed and bent down at right angles. These points form bearings which rest on two pieces of metal held in a retort stand. Metal clamps ("bossheads" or "collars") such as are used for fastening rings to stands are attached to the upper and lower ends of the rod and adjusted so that the pendulum beats seconds. The shadow of this pendulum, or of a cardboard pointer attached to it, may be thrown on the screen by a single reflection of a beam of light from the side of the lantern house. No lenses are required either for this or for the clock described in the preceding paragraph.

EXPERIMENTS.

I. Absence of Supersaturation in Solutions of Liquids in Liquids. A good lecture experiment to illustrate this point may be made with a mixture of phenol and water. A flat capillary tube containing water, shaken up with about 20 percent by volume of phenol, is placed alongside the projection thermometer in the lantern cell. When the temperature is gradually raised and lowered the tube becomes suddenly transparent and opaque alternately, at practically the same temperature, as the saturation point is passed. The capillary tube should be about 3 mm. wide by 0.5 mm. thick, inside dimensions. Such tubes may be made by flattening a bulb with a pair of tongs, reheating, and pulling out.

The difficulty of obtaining supersaturated solutions of liquids in liquids has been noted by several observers (Rothmund,[1] Füchtbauer,[2] Fawcett[3]). Füchtbauer suggests that dust particles, which are probably amorphous, act as nuclei for liquids and not for crystalline substances. He himself, however, observed that purification of the liquid made very little, if any, difference. Fawcett obtained similar results. It is possible that the cause of the small degree of supersaturation of liquids is connected with the comparatively small surface tension of the interface between liquid and liquid. At any rate, the following calculations in two typical cases, for which data are available, are of interest. Taking the surface energy of the interface gypsum-saturated solution as 550 ergs per sq. cm.,[4] and assuming arbitrarily the radius of the particles initially formed to be 15 $\mu\mu$ (0.0000015 cm.),[5] a simple calculation shows that, for equilibrium, the solution would have to be about six times as strong as the normally saturated solution. This is probably well beyond the limit of supersaturation actually relizable. On the other hand, in the case of isobutyric acid and water, the surface energy of whose interface is 1.76 ergs, particles of the acid with a radius

[1] Zeit. phys. Chem., 26, 444 (1898).

[2] Zeit. phys. Chem., 48, 566 (1904).

[3] Proc. Roy. Soc. Canada, 1913.

[4] Hulett, Zeit. phys. Chem., 37, 404 (1901). A slip in the calculation of this value was corrected by Freundlich, "Capillarchemie," 1909, p. 144, but Freundlich takes Hulett's value for the diameter of the particles instead of the radius. With this additional correction the value is 550.

[5] 15 $\mu\mu$ is the thickness of the black spot in a soap bubble. This value is also within the limits of the various experimentally determined thicknesses of films of matter which show the properties of the substances in mass.

of 15 $\mu\mu$ would be in equilibrium with a solution only 0.8 percent stronger than the normally saturated solution. At the ordinary temperature this corresponds to a change of temperature of about 0.5°.[6] Since it is very difficult to determine accurately the temperatures at which turbidity appears and disappears—the identity of which is the usual criterion for absence of supersaturation—a difference of this order of magnitude might easily escape observation.

II. Superheating of Liquids. It is very easy to superheat liquids in small, clean tubes. When a liquid begins to boil, the ebullition usually takes place quite locally, either at a few fixed points on the walls of the vessel or from particles suspended in the liquid from which streams of bubbles may be seen rising. The smaller the vessel and the smaller the volume of the liquid the less is the chance of the presence of these starting-points for bubbles. It appears, moreover, that there is a gradation in the effectiveness of the nuclei present—*i. e.,* some will cause ebullition when the liquid is slightly superheated, while others will not become effective until the liquid is heated to a higher temperature—for the smaller the tube the higher is the temperature to which the liquid can be heated without boiling. This is in accordance with the law of probability; the nuclei of medium effectiveness are the most abundant, and therefore, on decreasing the size of the tube, the most (and least) effective nuclei are the first to disappear. This may be shown in the projection cell by gradually heating simultaneously three glass tubes (0.7 mm., 1.5 mm. and 3 mm. internal diameter) half filled with ether. The largest tube may be heated to about 60°, when suddenly either all or part of the ether jumps out of the tube. In the second tube the ether does not explode until the temperature has risen many degrees higher, while the smallest tube may often be heated to over 90° without the hyperbasis being relieved, although the ether may be seen to be evaporating with great rapidity at the free surface.

The effect of the insertion of a fine capillary tube, open at the lower end, may be shown in the larger tube of ether, superheated to about 50°. Also the effect of a grain of pipe clay and of a platinum wire may be demonstrated in the same tube. The latter

[6] Alexjew, Wied. Ann. 28, 305 (1886).

causes a temporary disturbance, but generally loses its effectiveness after a few seconds.

It is interesting to note that, if the same assumption be made as in the previous experiment as to the initial size of the bubbles (15 $\mu\mu$), and if the surface energy of ether at 90° is taken as 9 ergs,[7] a calculation of the pressure in the bubbles gives a value of about 12.5 atmospheres. This corresponds to a temperature of about 130° (extrapolated).

III. Linear Rate of Crystallisation. The relation between temperature and linear rate of crystallisation may be shown with melted vanillin. A thin-walled capillary tube about 1 mm. in diameter containing solidified vanillin is immersed in the projection cell to within about 3 cm. of the bottom, and boiling water run through the cell. This melts all the vanillin below the surface of the water, but leaves a quantity of unmelted solid in the upper end of the tube. The water is then cooled to about 75°, and the tube pushed down further into the cell and held in position against the thermometer scale with a cork wedge. At the same time the second pendulum described in paragraph 4 is set in motion. The rate of crystallisation is measured by the number of marks on the thermometer traversed by the edge of the solid during 20 seconds. The temperature of the cell is lowered by about 5° at a time, and successive readings of rate and temperature are taken as the crystallisation proceeds. If the lantern has a vertical attachment the relation between rate and temperature may be plotted on smoked glass and shown on the screen after each measurement. By timing the intervals properly, a complete curve showing the initial increase in rate below the melting point, the interval of constant rate, and the final decrease in rate with falling temperature, may be plotted on the glass before the crystallisation has reached the end of the tube. The measurements cannot be made below about 37°, since spontaneous crystallisation from nuclei begins at this temperature.

IV. Nuclei and Crystallisation. The relation between the number of nuclei and the temperature and duration of supercooling may be shown by Tammann's "exposure and development" method.[8] A double projecting cell is used, each section

[7] Ramsay and Shields, Zeit. phys. Chem., **12**, 442 (1893).
[8] Zeit. phys. Chem., **25**, 441 (1898).

of which may be heated and cooled rapidly. Vanillin (MP = 81°) is the most satisfactory substance to use for these experiments. A flattened capillary tube, about 2 mm. x 0.5 mm. inside dimensions, is filled with vanillin, melted in one side of the cell in boiling water, quickly transferred to the other half of the cell, at (say) 20°, and "exposed" for a definite number of seconds (say 5), as shown by the shadow of the pendulum, and finally put back quickly into the first cell, which in the meantime has been cooled to a suitable "development" temperature (60°). It is easier to count the nuclei if the tube is put back into the cold half of the cell immediately they begin to appear; this checks the otherwise too rapid growth. The temperature and time of exposure may, of course, be varied.

For these experiments it is convenient to arrange the four tubes conducting hot and cold water to the two halves of the cell so that they pass through four spring pinch-cocks, fixed in a row on a board. By this means the temperatures of the two parts of the cell may be controlled by the four fingers of one hand, thus leaving the other hand free to manipulate the capillary tube.

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Comparative Sec. Area for same V. drop	1.	3.8	.00203	.00375	.0119
Weight: lbs. per cu. in.	.0574	.0564	.320	.090	.280
Tensile strength, lbs. per sq. in.	*800 to 1,000	*1,000 to 1,500	20,000 to 30,000	24,000 to 30,000	30,000 to 50,000
Temp. of oxidation in air	640° C.	500° C.	...	...	...

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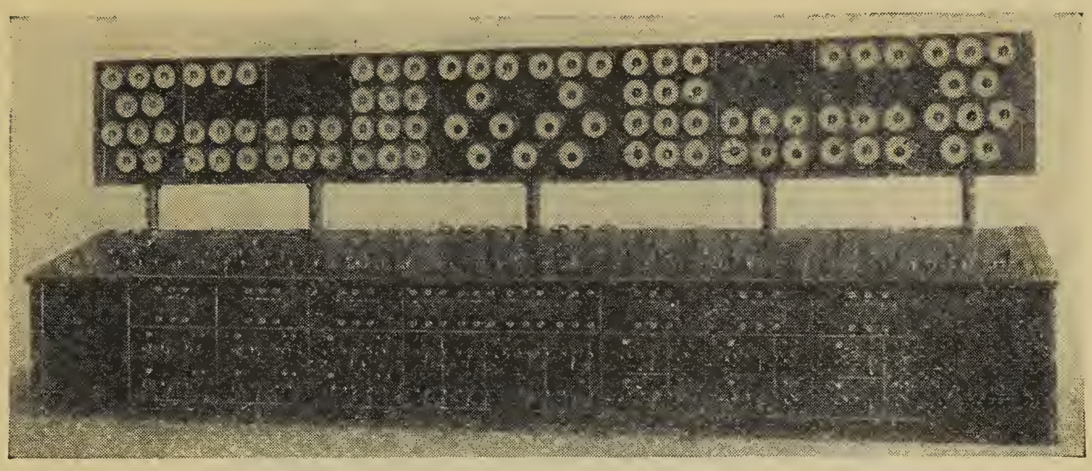

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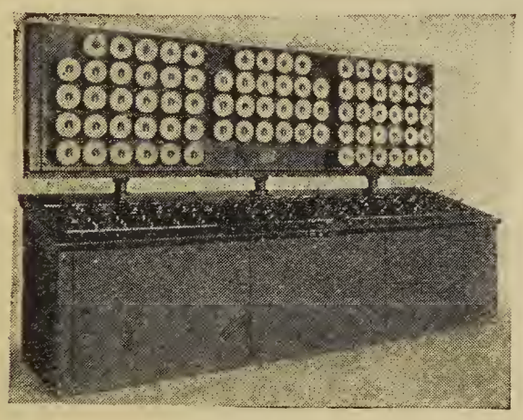
Fig. 2. Shows control desk for the receiving station; it controls two 115,000 volt incoming lines; four banks of three each 4000 kva., 115,000/11,000 volt transformers; two 800 amperes, 11,000 volt tie-in lines; four 800 amperes, 11,000 volt out-going lines; four 400 amperes, 11,000 volt out-going lines, and two local service transformers.



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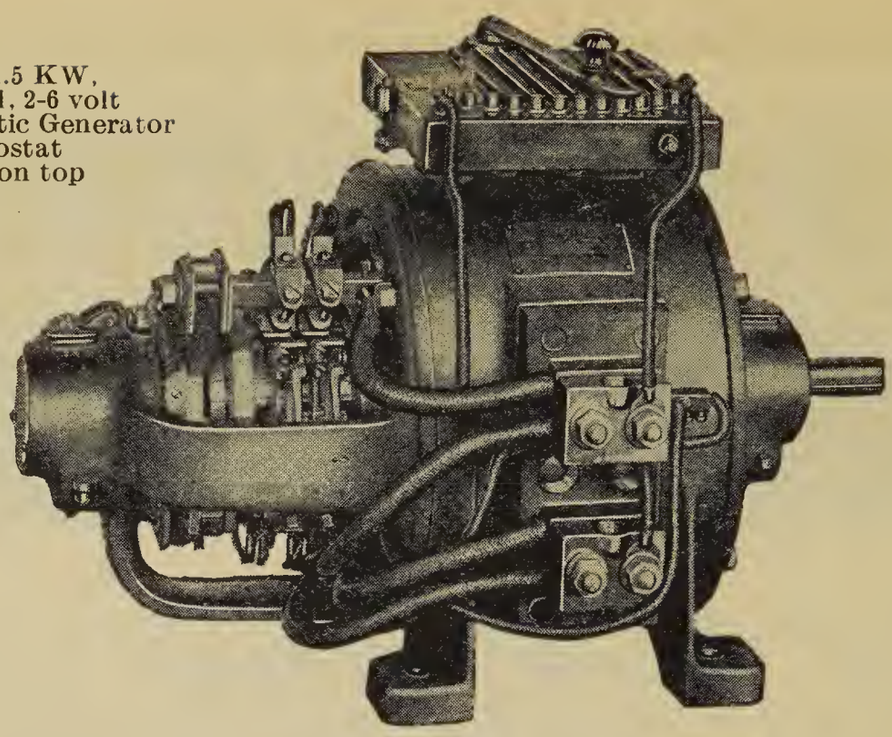

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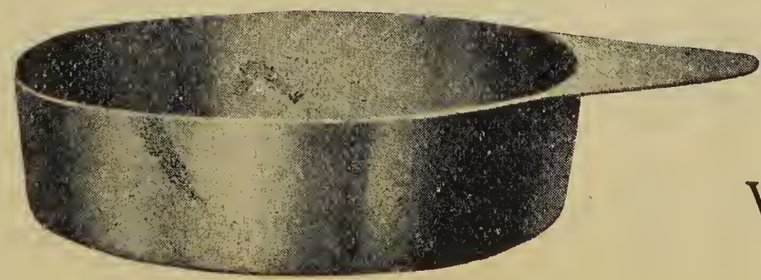

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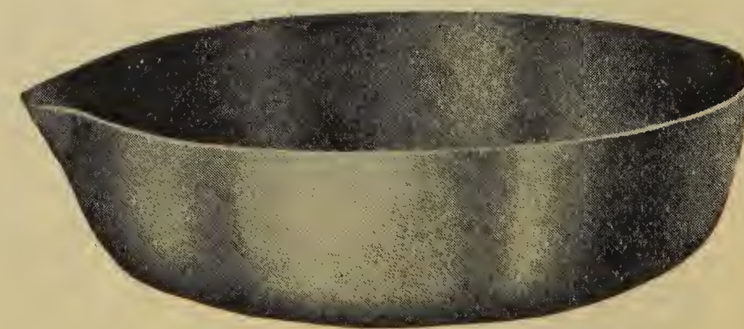

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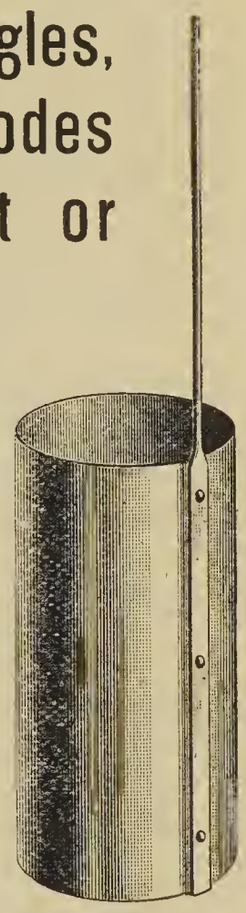

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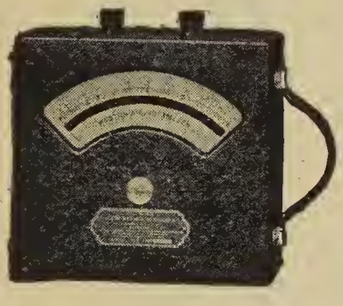

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